Notes

Synthesis of Seven-Coordinate (Catecholato)bis-(aminoethanethiolato)oxomolybdenum(VI) Complexes

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Because of their intrinsic relevance to the active sites of molybdoenzymes, the chemistry of oxomolybdenum complexes involving NS donor ligands has received the intense attention of coordination chemists and numerous papers in this area have been published[1].

Recently we studied on oxomolybdenum complexes of N-salicylidene-2-aminophenolate[2], N-salicylidene-2-aminobenzenethiolate[3], and bis(hydroxyethyl)dithiocarbamate ligands[4] acting as the ONO, ONS, SS donors to stimulate many characteristic properties of the active sites of molybdoenzymes.

In this work, we report some new monomeric oxomolybdenum(VI) complexes containing two aminoethanethiolate and one of five different catecholate ligands. The synthesis and spectroscopic properties of the complexes are also discussed.

Experimental

Measurement. Elemental analyses were performed by Kolon R & D center. Molybdenum was determined gravimetrically as lead molybdate by literature method[5]. The M.P. measurements were performed by using a Haake melting point apparatus. Electron-impect-ionization mass spectra were obtained by Kratos MS-25 RFA spectrometer. Infrared spectra were recorded with a Mattson Polaris FT-IR spectrophotometer. ^{1}H and ^{13}C-NMR spectra in DMSO-d_6 were recorded on a Bruker AM-300 spectrometer and referenced to TMS (internal). Electronic absorption spectra were obtained on a Pye Unicam SP-800 spectrophotometer.

Synthesis. All chemicals used in synthesis were of reagent grade and were used without further purification. The starting material $MoO_2(aet)_2$, where aet is aminoethanethiolate, was prepared by literature method[6].

[MoO(X-cat)(aet)$_2$]. For X-cat=catecholate(cat), 4-methylcatecholate(CH_3-cat), 2,3-dihydroxynaphthalene(Naph-cat), 4-Nitrocatecholate(NO_2-cat), and tetrachloro-1,2-benzoquinone (Cl_4-cat), the preparative procedure used was examplefied by that for [MoO(cat)(aet)$_2$].

Catechol (0.16 g, 5 mmol) was added to a solution of MoO_2 (aet)$_2$ (0.40 g, 4.8 mmol) in methanol (10 ml) to give an immediate brown solution. The solution was stirred at room temperature for 2 hr and was allowed to stand in refrigerator for 3 days. A redish-brown crystalline was collected by filtration, then washed several times with methanol and diethylether and dried under vacuum oven.

Analytical and yield data were as follows;

[MoO(cat)(aet)$_2$]. Brown, Yield: 77%, mp.: 200℃ (dec.). Anal. Calcd. for $C_{10}H_{16}N_2O_3S_2Mo$: Mo, 25.77; C, 32.26; H, 4.33; N, 7.32. Found: Mo, 26.04; C, 32.30; H. 4.35; N, 7.05. MS (EI): m/e=372. IR (KBr, cm^{-1}): 889 (Mo=O_t), 3278, 3224, 3144 (N-H). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 2.79-2.93 (2H, m, CH_2), 3.01 (2H, t, CH_2), 6.07-6.33 (4H, m, C_6H_4). ^{13}C-NMR (75.5 MHz, DMSO-d_6): δ 32.13, 32.18, 45.60, 47.75, 112.01, 112.15, 113.15, 116.67, 156.12, 157.61. UV-vis. (log ε) in DMSO, nm: 258 (3.77), 280 (3.78), 356 (3.52).

[MoO(CH_3-cat)(aet)$_2$]. Redish-brown, Yield: 83%, mp.: 177℃ (dec.). Anal. Calcd. for $C_{11}H_{18}N_2O_3S_2Mo$: Mo, 24.83; C, 34.20; H, 4.70; N, 7.25. Found: Mo, 23.84; C, 33.51; H. 4.57; N, 7.06. IR (KBr, cm^{-1}): 889 (Mo=O_t), 3275, 3223, 3144 (N-H). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 1.95 (3H, s, CH_3), 2.09 (3H, s, CH_3), 2.87 (2H, m, CH_2), 3.02 (2H, t, CH_2), 5.90-6.23 (3H, m, C_6H_3). UV-vis. (log ε) in DMSO, nm: 258 (3.95), 283 (3.90), 355 (3.66).

[MoO(Naph-cat)(aet)$_2$]. Redish-brown, Yield: 63%, mp.: 170℃ (dec.). Anal. Calcd. for $C_{14}H_{18}N_2O_3S_2Mo$: Mo, 22.72; C, 39.81; H, 4.30; N, 6.63. Found: Mo, 22.85; C, 39.59; H. 4.30; N, 6.42. MS (EI): m/e=422. IR (KBr, cm^{-1}): 889 (Mo=O_t), 3276, 3224, 3143 (N-H). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 2.86 (2H, m, CH_2), 3.02 (2H, t, CH_2), 6.54-7.40 (6H, m, $CH_{10}H_6$). UV-vis. (log ε) in DMSO, nm: 259 (4.51), 337 (3.96).

[MoO(NO_2-cat)(aet)$_2$]. Redish-brown, Yield: 91%, mp.: 204℃ (dec.). Anal. Calcd. for $C_{10}H_{15}N_3O_5S_2Mo$: Mo, 22.99; C, 28.78; H, 3.62; N, 10.07. Found: Mo, 22.73; C, 27.51; H. 3.49; N, 9.74. IR (KBr, cm^{-1}): 889 (Mo=O_t), 3276, 3223, 3143 (N-H). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 2.88 (2H, t, CH_2), 3.05 (2H, t, CH_2), 6.15-7.52 (3H, m, C_6H_3). UV-vis. (log ε) in DMSO, nm: 269 (4.08), 337 (3.81), 459 (4.22).

[MoO(Cl_4-cat)(aet)$_2$]. Brown, Yield: 67%, mp.: 300℃ Anal. Calcd. for $C_{10}H_{12}N_2O_3S_2Cl_4Mo$: Mo, 18.81; C, 23.55; H, 2.37; N, 5.49. Found: Mo, 18.80; C, 23.02; H. 2.30; N, 5.50. MS (EI): m/e=509. IR (KBr, cm^{-1}): 890 (Mo=O_t), 3277, 3223, 3143 (N-H). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 2.93 (2H, t, CH_2), 3.12 (2H, t, CH_2). UV-vis. (log ε) in DMSO, nm: 258 (4.18), 360 (sh), 532 (sh).

Result and Discussion

Synthesis. The complexes can be obtained by two synthetic routes[7]; i) oxidative addition of *o*-quinone to oxomolybdenum(IV), and ii) replacement of an oxo ligand by catechol on dioxomolybdenum(VI). But we, in this work, prepared all complexes by using route ii), because not all catechol ligands could be obtained in their quinone form and it was difficult to obtain oxomolybdenum(IV) complex, MoO(aet)$_2$. All complexes prepared were formulated on the basis of elemental analysis and a variety of physical measurements. The complexes were found to be stable in air in the solid state and highly soluble in DMSO and DMF, but insoluble in common other solvents.

Spectroscopic properties. The structures of all complexes were not determined, but we assumed that they are

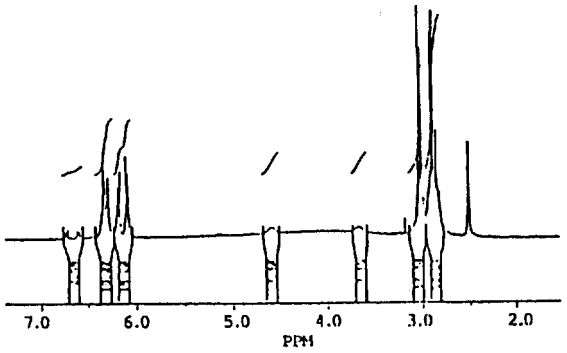


Figure 1. 300 MHz ^{1}H-NMR spectrum of [MoO(cat)(aet)$_2$] complex.

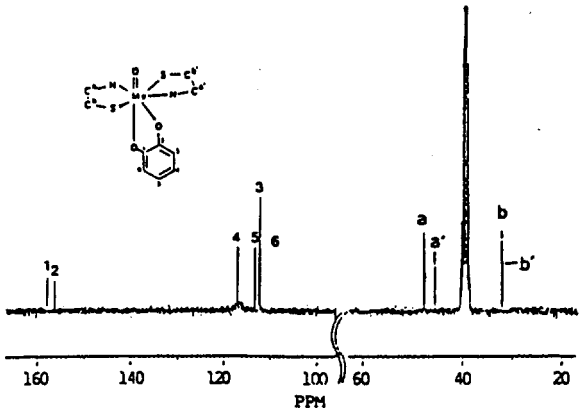


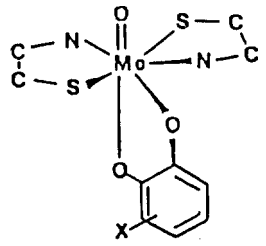
Figure 2. 75 MHz ^{13}C-NMR spectrum of [MoO(cat)(aet)$_2$] complex. The spectrum was assigned from ref. 10.

distorted pentagonal bipyramidals, where oxo group are bound terminally at one of the apicies, the two aminoethanethiolate (1-) groups are occupied four of the equatorial positions, and the catecholate (2-) ligand is spanned an equatorial and an apicial positions. This geometry is common for seven-coordinate monooxomolybdenum(VI) complexes[7,8].

The infrared spectra of these complexes all showed a sharp and intense band at ~890 cm^{-1}. These bands were assigned to the terminal molybdenum-oxygen stretching vibration, ν(Mo=O), by comparison with those of the parent compound[6] and the free ligands prepared in this work. These Mo=O stretching frequencies were lower than those (906-925 cm^{-1}) observed for seven-coordinate MoO^{+4} complexes, MoO(cat)(S$_2$CNEt$_2$)$_2$[7] and MoO(cat)(C$_5$H$_{10}$NO)$_2$[9]. This is attributed to be coordinate aminoethanethiolate instead of diethyldithiocarbamate / 1−piperidinolate, as I.R. spectra due to *cis*-MoO$_2$ group stretching vibration of MoO$_2$(aet)$_2$ in comparison with MoO$_2$(S$_2$CNEt$_2$)$_2$ (877, 910 cm^{-1}) and MoO$_2$(C$_5$H$_{10}$NO)$_2$ (901, 914 cm^{-1}) showed at 867, 890 cm^{-1}. The N-H stretching and bending frequencies of the aminoethanethiolate ligand each showed in the range of 3100-3300 cm^{-1} and ~1600 cm^{-1}. In general, the N-H stretching frequencies of the coordinated NH_2 group is higher than that of the free ligand (HSCH$_2$CH$_2$NH$_3$Cl, 2900 cm^{-1})[6]. Also, the S-H stretching vibration of the free ligand observed at ~2510 cm^{-1} exhibited no band in this region on complexation. This fact suggests that coordination occurs through the NH_2 group and ionized thiol group. For the coordination of catecholate ligand, a sharp intense bands due to C=C and C-O stretching vibration each appeared at ~1487 cm^{-1} and at ~1256 cm^{-1}. While the ligand can be coordinated as the quinone or semiquinone forms to the molybdenum, but we found that the ligand coordinate as catecholate because no bands at 1600-1700 cm^{-1} due to quinone or semiquinone forms of the ligand was observed[7].

The ^{1}H-NMR spectra of these compounds were devided into two regions, either site of a chemical shift of 5 ppm (downfield of Me$_4$Si). The catechol aromatic proton resonances appeared as multiplets in the low-field region. The high-field region comprised the aminioethanethiol resonances and intense singlets for 4-methyl group. The ^{1}H and ^{13}C-NMR spectra of [MoO(cat)(aet)$_2$] as shown in Figure 1 and 2.

Since ^{1}H- resonances appeared as unresolved multiplets but six ^{13}C resonances of the catecholate ligand were observed, the molecule does not possess any symmetry elements (*e.g.* C_2 axis). The ^{1}H resonances for the methylene group of aminoethanethiolate ligand each showed at ~3.01 ppm as triplet and in the range 2.79 to 2.93 ppm as multiplet, and amine resonances showed at 3.67 and 4.56 ppm. Also, four ^{13}C resonances for the methylene of aminoethanethiolates were observed (Figure 2). These data suggested that the two aminoethanethiolate ligands were not related to the mirror plane containing the catecholate plane and the Mo-O$_t$ axis. Thus, we think the molecular geometry adopts a structure such as (I) comparable with the mode of coordination of aminoethathiolate in MoO$_2$(aet)$_2$ complex.



(I)

Also, ^{1}H-NMR spectrum of [MoO(Me-cat)(aet)$_2$] exhibited integrated intensities for methyl, methylene, and aromatic protons in the ratio 3 : 8 : 3 consistent with the 1 : 2 stoichiometry of catechol and aminoethanethiol ligands. The ^{1}H resonances for the methyl of 4-methylcatecholate were observed at 1.95 and 2.09 ppm. These are attributed to the two possible geometric isomers for the compound when unsymmetrical cantecholate ligand are bound.[9,11]

The UV-visible spectra of these complexes each contain 3-absorption bands (258-532 nm). On the basis of the d^0 electronic configuration of metal, these transitions were assigned to L→M charge transfer[6,7] or catechole $\pi\rightarrow\pi^*$[9]. Mass spectra of [MoO(cat)(aet)$_2$], [MoO(Naph-cat)(aet)$_2$], and [MoO(Cl$_4$-cat)(aet)$_2$] complexes were obtaind, and each complex yielded its mass spectrum with a comparatively weak, but parent molecular ion.

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Aldehyde Syntheses from Carboxylic Acid Esters with Sodium Diethyldihexylaminohydroaluminate

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Sodium diethyldihydroaluminate (SDDA) is an interesting aluminohydride which reacts with equimolar secondary amines to give the corresponding amino derivatives.[2] Recently we have reported that sodium diethylpiperidinohydroaluminate (SDPA) is an excellent selective reducing agent for the synthesis of aldehydes from carboxylic acid esters.[3] Since diisobutyl aluminum hydride (DIBAH),[4] lithium tris(diethylamino)aluminum hydride[5] and diamino aluminum hydride[6] require very low temperature (−78℃)[4,5] or longer reaction time at elevated temperature (65℃),[6] the excellent yields of aldehydes at 0℃ by SDPA would make SDPA an excellent alternative to these hydrides for the aldehyde syntheses from esters. However we have soon found some undesirable features of SDPA.[7] Although SDPA gives almost quantitative yields of aldehydes from aromatic esters, it gives moderate to good yields of aldehydes from aliphatic esters. SDPA reduces aldehydes only partially because hydride and piperidyl group attack the carbonyl carbon competitively. The reduction of aldehydes and ketones which have α-hydrogen with SDPA accompanies hydrogen evolution (enolization). In order to improve these undesirable feature of SDPA, we explored several other amino derivatives of SDDA, and found sodium diethyldihexylaminohydroaluminate (SDHA) is a better selective reducing agent.

Table 1. Reduction of Ester and Carbonyl Compounds with *sec*-Amine Derivatives of SDDA at 0℃[a,b]

Reactants	Products	SDPyA	SDPA	SDEA	SDHA	SDBA
Ethyl benzoate	Benzaldehyde	95%	98%	95%	94%	63%
Benzaldehyde	Benzyl alcohol	48%	50%	62%	90%	90%
Acetophenone	1-Phenethyl alcohol	47%	50%	77%	90%	90%

[a]Reactions were run in 1.0 mmol scale (0.2 M in compound) for 1 h at 0℃ in THF-toluene and 1.1 mmol of hydride was added to compound. [b]Yields were determined by GLC.

We examined pyrrolidine, dibenzylamine, dihexylamine and diethylamine derivatives of SDDA, in the hope to find out the steric effect of amino group on the competition of hydride and amino group. The results are summarized in Table 1. As shown in Table 1, the competition of amino group in the reduction of aldehydes and ketones was dramatically decreased with bulky dihexylamine and dibenzylamine derivatives, however sodium diethyldibenzylaminohydroaluminate (SDBA) gave only a 63% yield of benzaldehyde from ethyl benzoate compared with a 94% yield by sodium diethyldihexylaminohydroaluminate (SDHA). Enolization of acetophenone by SDHA was also only 10% in contrast to 50% by SDPA. Therefore we tested the aldehyde syntheses from the representative aromatic and aliphatic esters with SDHA. As shown in Table 2, SDHA showed equally good results from aromatic esters, however unlike SDPA, SDHA competitively reduced nitro group as easily seen by the color change.[7] On the other hand, SDHA showed much improved yields from aliphatic esters such as ethyl caproate and phenyl caproate. Ethyl pivalate, a hindered ester, was also reduced by SDHA in an excellent yield, however ethyl cyclohexanecarboxylate and ethyl cyclohexylacetate, to our surprise, gave only moderate yields. These yields (48% and 67%) are even lower than those (59% and 78%) obtained by SDPA.[3] This suggested that these cyclohexane derivatives might be reduced to aldehydes satisfactorily by even smaller amino derivatives, SDPyA. We obtained much improved yields (77% and 96%) by SDPyA. However in the case of ethyl cinnamate, neither SDHA nor SDPyA improved the poor yield obtained by SDPA.[8] Sodium diethyldiethylaminohydroaluminate (SDEA) showed a slightly better yield (42%). In conclusion, SDHA is a good alternative of SDPA especially for the aldehyde syntheses from aliphatic esters, and SDPyA is useful for cyclohexane derivatives.