

- Abel, Pergamon Press, Oxford (1982).  
 12. R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).  
 13. I. Ugi, D. Marquarding, H. Klusacek, and P. Gillespie,

- Acc. Chem. Res.*, **4**, 288 (1971).  
 14. P. Meakin, J. P. Jesson, F. N. Tebbe, and E. L. Muetterties, *J. Am. Chem. Soc.*, **93**, 1797 (1971).

## Synthesis and Characterization of Molybdenum(V) Complexes with Tridentate Schiff Bases

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Six-coordinate molybdenum(V) complexes  $X[\text{MoO}(\text{NCS})_2(\text{L})]$ , where  $X = \text{PyH}^+$ ,  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ ,  $n\text{-Bu}_4\text{N}^+$ , and  $\text{L}$  = the tridentate schiff base dianions derived from the condensation reaction between various salicylaldehydes and 2-aminophenol have been synthesized. The complexes have been characterized by elemental analysis, conductivity, UV-visible, IR,  $^1\text{H-NMR}$ , and mass spectroscopy. The coordination around the molybdenum appears to be distorted octahedral. A tridentate ligand containing the ONO donor atoms occupies meridional positions with the N atom trans to the terminal oxo group. Two NCS ligands bond to the molybdenum through the N atom and are *cis* to the  $\text{Mo}=\text{O}_t$  group. The electrochemical behaviors of the complexes have also been investigated by cyclic voltammetry in dimethylsulfoxide.

### Introduction

Extensive studies have been carried out on oxomolybdenum(V) complexes of schiff base ligands.<sup>1</sup> In marked contrast, complexes with tridentate type ligands derived from salicylaldehyde and 2-aminophenol have been little studied. Recently, Yamanouchi *et al.*<sup>2</sup> reported the preparation and a single crystal X-ray structure determination for the type of complex  $(\text{PyH})[\text{MoOCl}_2(\text{sap})]$ , ( $\text{sap} = \text{N-salicylidene-2-aminophenol}$ ), and Mondal *et al.*<sup>3</sup> reported the preparation and electrochemical characterization of the complexes  $[\text{MoO}(\text{sap})(\text{cat})]$  ( $\text{cat} = \text{catechole}$ ) starting from  $[\text{MoO}_2(\text{sap})_2]$ . However, the oxomolybdenum(V) complexes of the mixed ligands with the isothiocyanate and N-salicylidene-2-aminophenol or its derivatives are not as yet reported. Mazzi<sup>4,5</sup> prepared also the rhenium(V) complexes,  $[\text{ReOCl}_n(\text{sap})]^-$  ( $n = 2, 3$ ) and  $[\text{ReO}(\text{L}^1)(\text{L}^2)]$  ( $\text{L}^1 = \text{sap}^{2-}$ ,  $\text{L}^2 = \text{monobasic bidentate ligands}$ ) depending on the stoichiometric ratios and conditions. These ligands contain potentially coordinating donor atom sets ON or ONO. It is known that the possibility of obtaining complexes with a particular structure is governed by the nature of the metal, the substituents and donor atom in the ligand, and the preparation conditions. Thus, with the aim of finding other possible stable configuration around molybdenum(V) containing the  $\text{MoO}^{3+}$  core, we have synthesized a series of complexes with isothiocyanates  $(\text{PyH})[\text{MoO}(\text{NCS})_2(\text{X-sap})]$ , where  $\text{X-sap}$  = the dibasic tridentate N-salicylidene-2-aminophenol or its 5-Me, 3-MeO, 3-EtO, or 5,6-Bz derivative, for the first time. In this paper, we report the syntheses, the structural determination by spectroscopic studies, and electrochemical behaviors of oxomolybdenum(V) complexes with the ligands illustrated (Figure 1).

### Experimental

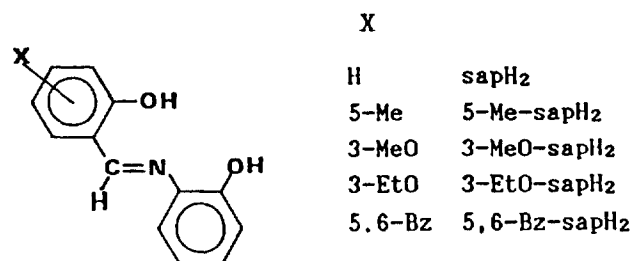


Figure 1. Ligands used.

**Materials.** All chemicals used in synthesis were of reagent grade and were used without further purification. Pyridinium oxoisothiocyanatomolybdate(V),  $(\text{PyH})_2[\text{MoO}(\text{NCS})_5]$ <sup>6</sup> and 5-methylsalicylaldehyde<sup>7</sup> were prepared by literature methods. All the schiff bases were prepared according to the method of Yamanouchi and identified by IR and  $^1\text{H-NMR}$ .<sup>2</sup> All solvents were dried by standard procedures<sup>8</sup> and distilled before use.

**Physical Measurements.** Elemental analyses were carried out by Kolon R and D center, and molybdenum was determined gravimetrically as lead molybdate by literature method.<sup>9</sup> M. P. measurements were performed by using a Haake melting point apparatus. The IR spectra of solid samples in KBr were recorded on a Mattson Polaris FT-IR. The  $^1\text{H-NMR}$  spectra in  $\text{DMSO-}d_6$  were recorded on a Bruker AM-300 spectrometer and referenced to TMS (internal). Electronic spectra were obtained on a Pye Unicam SP-800 spectrophotometer. Electron-impact-ionization mass spectra of thermally volatilized samples were obtained by the direct-insertion probe technique on a Kratos MS-25 RFA spectrometer. Molar conductance was measured with Metrohm 660 conductometer. Cyclic voltammograms were recorded on a PAR 273 Potentiostat/Galvanostat and PAR RE 0091 X-Y re-

corder. The electrochemical studies were conducted in oxygen free dimethylsulfoxide solutions containing 0.05 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. We employed a three-electrode cell configuration consisting of a Pt-wire working- and counter-electrode, and a saturated calomel reference electrode (SCE).

**Synthesis.** All reactions were carried out under an argon atmosphere with use of schlenk apparatus.

**(PyH)[MoO(NCS)<sub>2</sub>(L)](L=tridentate schiff bases).**

The same procedure was followed for all the complexes. Pyridiniumoxopentaisothiocyanatomolybdate(V) (10 mmol) in methanol (40 ml) was added to a suspension of an appropriate schiff base (10 mmol) in methanol (50 ml) with stirring at 50°C. After complete dissolution of an appropriate schiff base into the solution, pyridine (20 mmol) in 10 ml of methanol was slowly added to the solution to immediately give a precipitate of the desired compound. After the mixture was allowed to cool to room temperature, lustrous black crystals were collected by filtration, washed with a small amount of methanol and diethyl ether, dried in vacuum oven.

Analytical data for the complexes prepared as follows;

**(PyH)[MoO(NCS)<sub>2</sub>(sap)].** Yield: 77%, mp. 242-243°C. Molar conductance (Mho cm<sup>2</sup> mol<sup>-1</sup>, 10<sup>-3</sup> M in DMSO, 25°C): 53. Anal. Calcd for C<sub>20</sub>H<sub>15</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>Mo: C, 46.24; H, 2.91; N, 10.78; Mo, 18.48. Found: C, 45.40; H, 2.79; N, 10.31; Mo, 18.90. IR(KBr, cm<sup>-1</sup>): 848(ν<sub>C-S</sub>), 941(ν<sub>Mo=O</sub>), 1597(ν<sub>C=N</sub>), 2045(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 6.84-7.79(m, 8H, Ar-H), 8.10(s, 2H, *m*-C<sub>5</sub>H<sub>6</sub>N), 8.63(s, 1H, *p*-C<sub>5</sub>H<sub>6</sub>N), 8.92(s, 2H, *o*-C<sub>5</sub>H<sub>6</sub>N), 9.25(s, 1H, N=CH). UV-vis.(ε) in DMSO, nm: 309(4.26), 350(3.94), 422(3.71), 651.

**(PyH)[MoO(NCS)<sub>2</sub>(5-Me-sap)].** Yield: 80%, mp. 210-212°C. Molar conductance (Mho cm<sup>2</sup> mol<sup>-1</sup>, 10<sup>-3</sup> M in DMSO, 25°C): 50. Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>Mo: C, 47.28; H, 3.21; N, 10.50; Mo, 17.98. Found: C, 48.66; H, 3.39; N, 9.82; Mo, 17.98. IR(KBr, cm<sup>-1</sup>): 847(ν<sub>C-S</sub>), 940(ν<sub>Mo=O</sub>), 1610(ν<sub>C=N</sub>), 2046(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 2.30(s, 3H, 5-CH<sub>3</sub>-sap), 6.82-7.80(m, 7H, Ar-H), 8.10(s, 2H, *m*-C<sub>5</sub>H<sub>6</sub>N), 8.64(s, 1H, *p*-C<sub>5</sub>H<sub>6</sub>N), 8.93(s, 2H, *o*-C<sub>5</sub>H<sub>6</sub>N), 9.19(s, 1H, N=CH). UV-vis.(ε) in DMSO, nm: 311(4.24), 350(3.94), 420(3.63), 651.

**(PyH)[MoO(NCS)<sub>2</sub>(3-MeO-sap)].** Yield: 85%, mp. 217-218°C. Molar conductance (Mho cm<sup>2</sup> mol<sup>-1</sup>, 10<sup>-3</sup> M in DMSO, 25°C): 50. Anal. Calcd for C<sub>21</sub>H<sub>17</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Mo: C, 45.91; H, 3.12; N, 10.20; Mo, 17.46. Found: C, 44.48; H, 2.94; N, 9.54; Mo, 16.92. IR(KBr, cm<sup>-1</sup>): 865(ν<sub>C-S</sub>), 937(ν<sub>Mo=O</sub>), 1598(ν<sub>C=N</sub>), 2030(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 3.81(s, 3H, 3-CH<sub>3</sub>O-sap), 6.94-7.83(m, 7H, Ar-H), 8.09(s, 2H, *m*-C<sub>5</sub>H<sub>6</sub>N), 8.63(s, 1H, *p*-C<sub>5</sub>H<sub>6</sub>N), 8.93(s, 2H, *o*-C<sub>5</sub>H<sub>6</sub>N), 9.26(s, 1H, N=CH). UV-vis.(ε) in DMSO, nm: 319(4.29), 380(3.85), 440(3.53), 654.

**(PyH)[MoO(NCS)<sub>2</sub>(3-EtO-sap)].** Yield: 75%, mp. 203-204°C. Molar conductance (Mho cm<sup>2</sup> mol<sup>-1</sup>, 10<sup>-3</sup> M in DMSO, 25°C): 52. Anal. Calcd for C<sub>22</sub>H<sub>19</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Mo: C, 46.89; H, 3.40; N, 9.94; Mo, 17.03. Found: C, 45.68; H, 3.25; N, 9.45; Mo, 16.67. IR(KBr, cm<sup>-1</sup>): 835(ν<sub>C-S</sub>), 937(ν<sub>Mo=O</sub>), 1595(ν<sub>C=N</sub>), 2049(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 1.33(s, 3H, CH<sub>3</sub>CH<sub>2</sub>O-sap), 4.06(s, 2H, CH<sub>3</sub>CH<sub>2</sub>O-sap), 6.83-7.85(m, 7H, Ar-H), 8.09(s, 2H, *m*-C<sub>5</sub>H<sub>6</sub>N), 8.63(s, 1H, *p*-C<sub>5</sub>H<sub>6</sub>N), 8.92(s, 2H, *o*-C<sub>5</sub>H<sub>6</sub>N), 9.23(s, 1H, N=CH). UV-vis.(ε) in DMSO, nm: 318(4.25), 435(3.65), 644.

**(PyH)[MoO(NCS)<sub>2</sub>(5,6-Bz-sap)].** Yield: 81%, mp. 220

-221°C. Molar conductance (Mho cm<sup>2</sup> mol<sup>-1</sup>, 10<sup>-3</sup> M in DMSO, 25°C): 51. Anal. Calcd for C<sub>24</sub>H<sub>17</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>Mo: C, 50.62; H, 3.01; N, 9.84; Mo, 16.85. Found: C, 47.95; H, 3.05; N, 9.79; Mo, 16.80. IR(KBr, cm<sup>-1</sup>): 839(ν<sub>C-S</sub>), 936(ν<sub>Mo=O</sub>), 1592(ν<sub>C=N</sub>), 2041(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 6.82-8.79(m, 10 H, Ar-H), 7.87(s, 2H, *m*-C<sub>5</sub>H<sub>6</sub>N), 8.37(d, 1H, *p*-C<sub>5</sub>H<sub>6</sub>N), 8.82(s, 2H, *o*-C<sub>5</sub>H<sub>6</sub>N), 9.60(s, 1H, N=CH). UV-vis.(ε) in DMSO, nm: 344(4.18), 461(3.88), 633.

**(X<sub>4</sub>N)[MoO(NCS)<sub>2</sub>(3-MoO-sap)](X=Me, Et, and *n*-Bu).** (PyH)[MoO(NCS)<sub>2</sub>(3-MoO-sap)] (5 mmol) synthesized by following the procedure as mentioned above was dissolved in hot methanol (150 ml). To this solution added appropriate tetraalkylammonium salts (15 mmol) to immediately give a precipitate of the lustrous black crystals. The crystals were collected by filtration, washed well with ethanol, and dried in vacuum oven.

Analytical data for the complexes prepared as follows;

**(Me<sub>4</sub>N)[MoO(NCS)<sub>2</sub>(3-CH<sub>3</sub>O-sap)].** Yield: 60%, mp. 267-268°C. Anal. Calcd for C<sub>20</sub>H<sub>23</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Mo: C, 44.20; H, 4.27; N, 10.31; Mo, 17.67. Found: C, 45.39; H, 4.13; N, 10.12; Mo, 17.30. IR(KBr, cm<sup>-1</sup>): 867(ν<sub>C-S</sub>), 943(ν<sub>Mo=O</sub>), 1596(ν<sub>C=N</sub>), 2048(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 3.11(s, 12H, (CH<sub>3</sub>)<sub>4</sub>N), 3.81(s, 3H, 3-CH<sub>3</sub>O-sap), 6.84-7.82(m, 7H, Ar-H), 9.25(s, 1H, N=CH).

**(Et<sub>4</sub>N)[MoO(NCS)<sub>2</sub>(3-MeO-sap)].** Yield: 71%, mp. 247-248°C. Anal. Calcd for C<sub>24</sub>H<sub>31</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Mo: C, 48.07; H, 5.21; N, 9.34; Mo, 16.60. Found: C, 49.76; H, 5.27; N, 9.32; Mo, 15.50. IR(KBr, cm<sup>-1</sup>): 869(ν<sub>C-S</sub>), 939(ν<sub>Mo=O</sub>), 1596(ν<sub>C=N</sub>), 2048(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 1.17(s, 12H, (CH<sub>3</sub>CH<sub>2</sub>)<sub>4</sub>N), 3.21(s, 8H, (CH<sub>3</sub>CH<sub>2</sub>)<sub>4</sub>N), 3.81(s, 3H, 3-CH<sub>3</sub>O-sap), 6.84-7.83(m, 7H, Ar-H), 9.24(s, 1H, N=CH).

**(*n*-Bu<sub>4</sub>N)[MoO(NCS)<sub>2</sub>(3-MeO-sap)].** Yield: 71%, mp. 195-196°C. Anal. Calcd for C<sub>32</sub>H<sub>47</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>Mo: C, 53.99; H, 6.66; N, 7.87; Mo, 13.48. Found: C, 55.00; H, 6.81; N, 7.82; Mo, 12.12. IR(KBr, cm<sup>-1</sup>): 866(ν<sub>C-S</sub>), 938(ν<sub>Mo=O</sub>), 1597(ν<sub>C=N</sub>), 2051(ν<sub>C=N</sub>, NCS). <sup>1</sup>H-NMR(300 MHz, DMSO-*d*<sub>6</sub>): δ 0.94(s, 12H, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N), 1.58, 1.32(d, 16H, (CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N), 3.17(s, 8H, (CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>N), 3.81(s, 3H, 3-CH<sub>3</sub>O-sap), 6.82-7.81(m, 7H, Ar-H), 9.24(s, 1H, N=CH).

## Results and Discussion

The new oxomolybdenum(V) complexes with tridentate schiff bases are formed quickly, in high yield, from methanol solution. The tetraalkylammonium salts of [Mo(NCS)<sub>2</sub>(3-MeO-sap)]<sup>-</sup> ion are obtained from an excess methanol solution in the presence of three-fold molar excess of the appropriate tetraalkylammonium salts. All complexes are stable in air in the solid state and highly soluble in DMSO and DMF, but have very poor solubilities in MeOH and EtOH.

The values of molar conductance of the complexes are in the range 50 to 53 Mho cm<sup>2</sup> mol<sup>-1</sup> in DMSO solution, indicating that the complexes are 1:1 electrolytes. These values also fall into the range that Geary<sup>10</sup> and Greenwood *et al.*<sup>11</sup> have suggested. (50-70 Mho cm<sup>2</sup> mol<sup>-1</sup> as the range for 1:1 electrolytes in DMSO)

**IR Spectra.** A single strong absorption band, arising from the stretching vibration of the MoO<sup>3+</sup> group, is observed at near 930 cm<sup>-1</sup>. This frequency agrees with that usually observed for mono-oxocomplexes of molybdenum ions in distorted octahedral, indicating the presence of Mo=O bond.<sup>12</sup>

Schiff base ligands contain potentially coordinating donor atom sets ON or ONO, but IR spectra support dianionic tridentate ONO chelation of it. The  $\nu_{\text{OH}}$  band ( $\sim 3430 \text{ cm}^{-1}$ ) of the free ligands disappears on complexation, indicating coordination through the deprotonated phenolic oxygen atoms. The intense bands at ca.  $1630 \text{ cm}^{-1}$  associated with the C=N stretching frequency of the free ligands are shifted to ca.  $1600 \text{ cm}^{-1}$ , respectively, in the corresponding complexes, indicating the coordination of the azomethine nitrogen and the charged phenolic oxygen atom to the metal ion. Those results are in accordance with the assignments for the complex of the N-arylsalicylideneimines reported previously.<sup>13</sup> That is, when the schiff base is coordinated as an anionic ligand through both oxygen and nitrogen atoms, the  $\nu(\text{C}=\text{N})$  vibration shifts to lower frequency by ca.  $20 \text{ cm}^{-1}$ , whilst coordination as neutral species, through the nitrogen atom only, shifts this band to higher frequency.

In regard to the  $\text{NCS}^-$  ligands, their characteristic absorption frequencies clearly indicate the coordination through the N atom. The strong band resulting from the C=N stretching mode is observed in the range  $2050$  to  $2030 \text{ cm}^{-1}$ , much lower than the value (ca.  $2100 \text{ cm}^{-1}$ ) observed for the  $\text{SCN}^-$  ligand in the thiocyanato complex.<sup>14</sup> This frequency lowering is characteristic for the N-bonded  $\text{NCS}^-$  ligand. Also, the C-S stretching vibration is observed at relatively high frequencies,  $866$ - $835 \text{ cm}^{-1}$ —a typical feature for isothiocyanates.<sup>6,15</sup>

**<sup>1</sup>H-NMR Spectra.** The schiff base ligands possess two phenolic groups and an azomethine group. <sup>1</sup>H-NMR spectra in  $\text{DMSO}-d_6$  showed the aromatic protons as multiplet in the range  $6.79$ - $8.38 \text{ ppm}$  and OH protons of the two phenolic groups in the range  $9.60$ - $10.2 \text{ ppm}$  and  $13.33$ - $15.65 \text{ ppm}$ . The azomethine protons appeared as a sharp singlet in the range  $8.88$ - $9.60 \text{ ppm}$ . The complexes did not show any OH protons, and the azomethine protons of the free ligands are shifted to downfield ( $9.19$ - $9.69 \text{ ppm}$ ) on complexation. These observations suggest that the ligands of  $\text{sap}^{2-}$  coordinate to the molybdenum atom through the charged phenolic oxygen atoms and nitrogen atom of an azomethine group.

The methyl protons of  $(\text{PyH})(\text{MoO}(\text{NCS})_2(5\text{-Me-sap}))$  appeared as a singlet at  $2.30 \text{ ppm}$  and the methoxy protons of  $\text{X}[\text{MoO}(\text{NCS})_2(3\text{-MeO-sap})]$  ( $\text{X} = \text{PyH}^+$ ,  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$  and  $n\text{-Bu}_4\text{N}^+$ ) appeared as a singlet at  $3.81 \text{ ppm}$ . The methyl- and methylene-protons for the 3-EtO-sap ligand of  $(\text{PyH})[\text{MoO}(\text{NCS})_2(3\text{-EtO-sap})]$  appeared as a sharp singlet at  $1.33$  and  $4.06 \text{ ppm}$  with relative intensity 3:2.

The aromatic protons of the pyridinium ion as a counter ion are easily distinguished from those of  $\text{sap}^{2-}$  ligand by comparison of the spectra of the corresponding free ligands and those of the complexes containing  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ , and  $n\text{-Bu}_4\text{N}^+$  instead of  $\text{PyH}^+$  as a counter ion. The ortho-, meta- and para-protons for the pyridinium ion of all the complexes except  $(\text{PyH})[\text{MoO}(\text{NCS})_2(5,6\text{-Bz-sap})]$  appeared at near  $8.90$ ,  $8.10$ , and  $8.60 \text{ ppm}$  with relative intensity ratio of 2:2:1. The methyl- and methylene protons for the tetraethylammonium ion of  $(\text{Et}_4\text{N})\text{-}[\text{MoO}(\text{NCS})_2(3\text{-MeO-sap})]$  appeared at  $1.17$  and  $3.21 \text{ ppm}$ . The 4-n-tetrabutylammonium complex showed alkyl protons at  $0.94$  ( $-\text{CH}_3$ ),  $1.58$ ,  $1.32$  ( $-(\text{CH}_2)_2-$ ) and  $3.17 \text{ ppm}$  ( $\text{CH}_2\text{-N}$ ) with relative intensity of 3:2:2:2.

**Electronic Spectra.** The absorption bands for the oxomolybdenum(V) complexes can be assigned on the basis of

**Table 1.** Mass Spectral Data for the  $(\text{PyH})[\text{MoO}(\text{NCS})_2\text{L}]$  Complexes

L	Fragment	m/e <sup>a</sup>
sap	$\{(\text{PyH})[\text{MoO}(\text{NCS})_2(\text{sap})]\}^+$	519(521.42)
	$[\text{MoO}_2(\text{sap})]^+$	340(341.15)
	$[\text{MoO}(\text{sap})]^+$	324(325.15)
5-Me-sap	$[\text{MoO}_2(5\text{-Me-sap})]^+$	354(355.18)
	$[\text{MoO}(5\text{-Me-sap})]^+$	338(339.18)
3-MeO-sap	$[\text{MoO}_2(3\text{-MeO-sap})]^+$	370(371.18)
	$[\text{MoO}(3\text{-MeO-sap})]^+$	353(355.18)
3-EtO-sap	$[\text{MoO}_2(3\text{-EtO-sap})]^+$	384(385.21)
5,6-Bz-sap	$[\text{MoO}_2(5,6\text{-Bz-sap})]^+$	390(391.21)
	$[\text{MoO}(5,6\text{-Bz-sap})]^+$	374(375.21)

<sup>a</sup>Calculated values are given in parentheses.

**Table 2.** Cyclic Voltammetric Results<sup>a</sup> for  $(\text{PyH})[\text{MoO}(\text{NCS})_2\text{L}]$  Complexes in 0.05 M TBAP at 25°C

L	mV/sec	$E_{pc}$ , V (vs. SCE) <sup>b</sup>	
sap	100	-0.70	-1.10 (-0.99)
5-Me-sap	100	-0.64	-1.30 (-1.18)
3-MeO-sap	100	-0.64	-1.29 (-1.16)
3-EtO-sap	100	-0.63	-1.28 (-1.16)
5,6-Bz-sap	100	-0.67	-1.19 (-1.07)

<sup>a</sup>Solvent DMSO; solute concentration  $\sim 10^{-3} \text{ M}$ ; working electrode platinum; reference electrode SCE. <sup>b</sup>Values in parentheses are coupled oxidation peaks observed with complete CV cycle.

the energy levels reported by Sabet<sup>6</sup> for tetragonal oxo-complexes of  $d^1$  molybdenum ion. Generally three  $d-d$  transitions,  ${}^2\text{B}_2 \rightarrow {}^2\text{E}(d_{xy} \rightarrow d_{xz}, d_{yz})$ ,  ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1(d_{xy} \rightarrow d_{x^2-y^2})$ , and  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1(d_{xy} \rightarrow d_{z^2})$  are predicted in  $\text{C}_{4v}$  symmetry. But, of these  $d-d$  transitions, one weak and broad absorption band in the ligand field region (ca.  $650 \text{ nm}$ ) due to the first crystal field transition  ${}^2\text{B}_2 \rightarrow {}^2\text{E}$  is observed in the electronic spectra of the complexes reported in this work. Both of the absorption bands arising from  ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$ , and  ${}^2\text{B}_2 \rightarrow {}^2\text{A}_1$  are obscured by very weak nature or overlap of other higher intense charge transfer transitions.<sup>17</sup> On the other hand, the bands observed at below  $461 \text{ nm}$  are probably due to  $\text{L} \rightarrow \text{M}$  or  $\text{M} \rightarrow \text{L}$  charge transfer transitions.<sup>18</sup>

**Mass Spectrometry.** The dominant metal-containing ions and m/e values for all the complexes are presented in Table 1. The m/e values quoted are calculated for the most abundant isotope, <sup>98</sup>Mo. Each of these peaks exhibited an isotope distribution pattern characteristic of molybdenum, respectively. The molecular ion peak of  $(\text{PyH})[\text{MoO}(\text{NCS})_2(\text{sap})]$  is observed at m/e 519. The fragment corresponding to loss of the pyridinium ion and isothiocyanate ligands from  $(\text{PyH})[\text{MoO}(\text{NCS})_2(\text{sap})]$  is observed at m/e 324. The peak corresponding to  $[\text{MoO}_2(\text{sap})]^+$ , which reflects the strong oxygen affinity of the electropositive  $\text{MoO}^{4+}$  center is observed at m/e 340. All complexes yielded fragments due to  $[\text{MoO}(\text{sap})]^+$  and  $[\text{MoO}_2(\text{sap})]^+$ , but molecular ion peak due to each formula of the complexes except  $(\text{PyH})[\text{MoO}(\text{NCS})_2(\text{sap})]$  was not observed in these work conditions.

**Electrochemistry.** The electrochemical behaviors of the oxomolybdenum(V) complexes in  $\text{DMSO}/0.05 \text{ M TBAP}$



- Inorg. Chim. Acta.*, **7**, 365 (1973).
- B. S. Furniss, A. J. Hannaford, P. W. G. Smith, and A. R. Tatchell, "Vogel's Textbook of Practical Organic Chemistry", 5th ed., Longman, London, p. 983, 1988.
  - D. D. Perrin and W. L. Armarego, "Purification of Laboratory Chemicals", 3rd ed., Pergamon Press, Oxford, 1988.
  - J. Basset, R. C. Denney, G. H. Jeffrey, and J. Mendharn, "Vogel's Textbook of Quantitative Inorganic Analysis", 4th ed., Longman, New York, U.S.A., p. 471, 1978/
  - W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
  - N. N. Greenwood, B. P. Straughan, and A. E. Wilson, *J. Chem. Soc., A*, 2209 (1968).
  - (a) P. C. H. Mitchel, *Coord. Chem. Rev.*, **1**, 315 (1966); (b) M. Chaudhury, *Inorg. Chem.*, **24**, 3011 (1985).
  - (a) W. E. Hill, N. Atabay, C. A. McAuliffe, F. P. McCullough, and S. M. Razzolci, *Inorg. Chim. Acta.*, **35**, 35 (1979); (b) S. Chandra and K. K. Sharma, *Transition Met. Chem.*, **9**, 1 (1984).
  - K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., John Wiley and Sons, New York, p. 187, 1970.
  - A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).
  - K. Biemann, "Tables of Spectral Data for structure Determination of Organic Compounds", 2nd ed., Springer-Verlag, New York, 1989.
  - (a) S. Purohit, A. P. Kolay, L. S. Prasad, P. T. Manoharan, and S. Ghosh, *Inorg. Chem.*, **28**, 3735 (1989); (b) A. Symal and M. A. Bari Niazi, *Transition Met. Chem.*, **10**, 54 (1985).
  - (a) M. Chaudhury, *J. Chem. Soc. Dalton Trans.*, 115 (1984); (b) F. W. Moore and R. E. Rice, *Inorg. Chem.*, **7**, 2511 (1968).
  - A. Marchi, A. Duatti, R. Rossi, L. Magon, R. Pasqualini, V. Bertolasi, V. Ferretti, and G. Gilli, *J. Chem. Soc. Dalton Trans.*, 1743 (1988).
  - S. J. Lippard, "Progress in Inorganic Chemistry", 1st ed., John Wiley and Sons, New York, U.S.A., Vol. 22, p. 57, 1977.

## Kinetics and Mechanisms of the Oxidation of Carbon Monoxide on $\text{Eu}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$ Perovskite Catalysts

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The catalytic oxidation of CO on perovskite  $\text{Eu}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$  has been investigated at reaction temperatures from 100 to 250°C under stoichiometric CO and O<sub>2</sub> partial pressures. The microstructure and Sr-substitution site of the catalyst were studied by means of infrared spectroscopy. The reaction rates were found to be correlated with 1.5- and 1.0- order kinetics with and without a CO<sub>2</sub> trap, respectively; first- and 0.5-order with respect to CO and 0.5-order to O<sub>2</sub> with the activation energy of 0.37 eV mol<sup>-1</sup>. It was found from IR,  $\sigma$  and kinetic data that O<sub>2</sub> adsorbs as an ionic species on the oxygen vacancies, while CO adsorbs on the lattice oxygens. The oxidation reaction mechanism is suggested from the agreement between IR,  $\sigma$  and kinetic data.

### Introduction

Most metal oxides contain an excess oxygen or excess metal in their crystal structures. The catalytic activity of nickel oxide is due to excess oxygen<sup>1</sup> while that of zinc oxide is due to oxygen vacancies formed by the excess zinc metal.<sup>2-4</sup> The positive holes caused by the excess oxygen activate the reactant molecules and the anion vacancies due to the excess metal are responsible for the catalytic activity.<sup>5,6</sup> On the other hand, the catalytic activity of metal oxides on the oxidation of carbon monoxide varies with the amount of impurity doped in the oxide catalyst inducing the positive holes or anion vacancies.<sup>7-9</sup> The bulk structure of perovskite-type mixed oxide has been well characterized and the formations of oxygen vacancies and metal deficiencies are easily controlled by the incorporation of the foreign atoms without changing the fundamental structure.<sup>10</sup>

In this point of view, the perovskite-type  $\text{EuCoO}_3$  doped with Sr was selected, since the Sr doping may play an important role in the enhancement of the catalytic activity. We prepared  $\text{Eu}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$  catalysts with different atomic mole fraction of Sr and characterized them by X-ray diffraction analysis and infrared spectroscopy.

### Experimental

**Catalyst Preparation.** The  $\text{Eu}_{1-x}\text{Sr}_x\text{CoO}_{3-y}$  powder was prepared by mixing appropriate weights of  $\text{Eu}_2\text{O}_3$  (99.99%),  $\text{SrCO}_3$  (99.995%) and CoO from  $\text{Co}_3\text{O}_4$  (99.995%) powders all obtained from the Aldrich Co. in ethanol, stirring them for 96h to obtain a homogeneous dispersed powders, filtering and drying at 150°C, putting in a covered Pt crucible, firing in air at 1150°C for 96h, and then slowly cooling to room temperature. The sample powder was ball-milled for 3h, cal-