film) 2969, 2880, 1735, 1459, 1183, 1135 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.15 (t, J=5.9 Hz, 1H), 4.05 (t, J=4.3 Hz, 2H), 3.80-3.68 (m, 16H), 2.64 (d, J=13.8 Hz, 2H), 2.11 (d, J=13.1 Hz, 1H), 1.98-1.90 (m, 2H), 1.44-1.13 (m, 13H), 0.92 (t, J=6.9 Hz, 6H), 0.81 (t, J=7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.7, 14.9, 17.3, 17.5, 36.8, 41.2, 43.1, 44.2, 45.6, 47.2, 65.1, 68.7, 69.0, 70.6, 71.0 (2 carbons), 71.1, 71.2, 71.6, 171.8, 174.5. **8b**. White solid (40% yield); mp 78-80 ℃; IR (NaCl, film) 2966, 2878, 1734, 1470, 1177, 1118 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 4.14 (t, J=5.6 Hz, 1H), 4.04 (t, J=4.3 Hz, 2H), 3.82-3.63 (m, 20H), 2.65 (d, J=13.5 Hz, 2H), 2.11 (d, J=12.9 Hz, 1H), 1.98-1.90 (m, 2H), 1.44-1.13 (m, 13H), 0.93 (t, J=6.9 Hz, 6H), 0.83 (t, J=6.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 14.6, 14.9, 17.3, 17.4, 36.8, 41.2, 43.1, 44.2, 45.5, 47.1, 64.8, 68.8, 68.9, 70.5, 70.9, 71.0, 71.1, 71.2, 71.3, 71.6 (2 carbons), 171.7, 174.5.

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Synthesis of Cobalt(III) Complexes of N,N'-Bis (β-mercaptoethyl)-trans-2.5-dimethylpiperazine

Hyang Ju Kim and Moo-Jin Jun*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea

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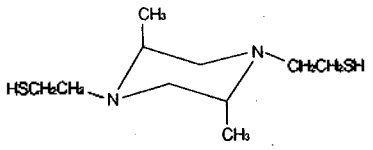
Various types of the metal complexes, monomeric, binuclear or tetranuclear metal complexes, with the tetradentate ligands containing the SNNS donor system have been known in the literature.[1,2]

In this work, a new SNNS-type ligand, N,N'-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine (H_2medpa) and the cobalt(III) complexes of medpa have been prepared. The medpa ligand can have both chair and boat conformations. A binuclear complex will be obtained if the lignad coordinates to a metal ion in the chair conformation, while a monomeric complex will be formed upon coordination of the ligand in the boat conformation (Figure 1). It is of interest to observe what type of metal complexes, monomeric or binuclear, would be obtained in this work.

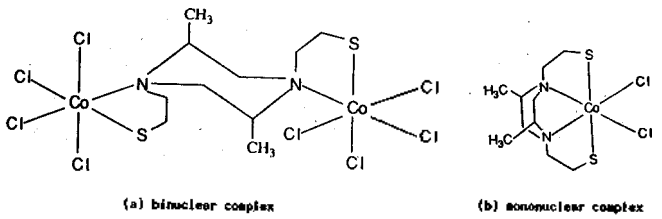


N,N'-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine (medpa)

Experimental

Preparation of N,N'-Bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine (H_2medpa). Ethylene sulfide (0.6 g, 0.1 mmol) in 10 mL of benzene was added slowly to a solution of trans-2,5-dimethylpiperazine (5.7 g, 0.05 mol) at 40 ℃ under nitrogen. After digesting for 2 hrs, the temperature of the reaction system was raised to 60 ℃, at which it was maintained for 24 hrs with stirring under nitrogen. The solution was cooled to room temperature, washed with water several times, and then throughly dried over $MgSO_4$. The solution was filtered and the solvent was removed by rotary evaporation. The pale yellow oil product was vacuum dried and kept under nitrogen. Yield: 1.9 g (16%).

Prepration of Sodium Octachloro[N,N'-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine]dicobaltate (III), $Na_4[Co_2(medpa)Cl_8]$. A solution of H_2medpa (1.2



(a) binuclear complex (b) mononuclear complex

Figure 1. Possible geometry of (a) $[Co_2(medpa)Cl_8]^{4-}$ and (b) $[Co(medpa)Cl_2]^-$ complexes.

g, 5 mmol) in 20 mL of methanol was slowly added to a suspeneded solution of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (3.6 g, 10 mmol) in 50 mL of methanol maintained at 60 ℃ under nitrogen. The resultant solution was allowed to stand at 60 ℃ for 1 hr. To this solution was added a solution of conc-HCl (3 mL) in 10 mL of methanol at 60-70 ℃, which was then allowed to stand for 5 hrs at 60-70 ℃. The hot solution was filtered and evaporated under reduced pressure. The precipitated product was dissolved in a mixed solution of methanol and water. Filtration and removal of the solvent by rotary evaporation (followed by vacuum to remove any solvent left), yielded a deep green product. Yield: 2.8 g (75%). Anal. Calcd. for $Na_4Co_2C_{10}H_{20}N_2S_2Cl_8$: C, 16.54; H, 2.76; N, 3.86; S, 8.84. Found: C, 16.81; H, 2.70; N, 3.75; S, 8.50.

Preparation of Sodium Octanitro[N,N′-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine]dicobaltate (III), $Na_4[Co_2(medpa)(NO_2)_8]$. 0.64 g (1 mmol) of $Na_4[Co_2(medpa)Cl_8]$ was dissolved in water and stirred with a magnetic stirrer at 65 ℃ for 30 min. 0.54 g (8 mmol) of $NaNO_2$ was added slowly to this solution and maintained at 65 ℃ for 3 hrs. The solution was filtered and evaporated under reduced pressure. The solid product was recrystallized from water and acetone. Yield: 0.3 g (57%). Anal. Calcd. for $Na_4Co_2C_{10}H_{20}N_{10}O_{16}S_2$: C, 14.82; H, 2.49; N, 17.29. Found: C, 14.78; H, 2.61; N, 16.40.

Preparation of Tetrakis(ethylenediamine)[N,N′-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine]dicobaltate(III) Perchlorate, $[Co_2(medpa)(en)_4](ClO_4)_4$. A solution of ethylenediamine (0.24 g, 4 mmol) in 10 mL of water was added slowly to a solution of $Na_4[Co_2(medpa)Cl_8]$ (0.64 g, 1 mmol) in 30 mL of water with stirring at 60 ℃. The temperature of the resultant solution was raised to 80 ℃, at which the solution was maintained for 5 hrs. The solution was filterd while hot, and 0.4 g of $NaClO_4$ was added to the filtrate, which was then evaporated under reduced pressure until precipitates were formed. The solid product was recrystallized from water and ethanol. Yield: 0.6 g (61%). Anal. Calcd. for $Co_2C_{18}H_{52}N_{10}S_2Cl_2O_{16}$: C, 23.29; H, 5.65; N, 15.09. Found: C, 23.20; H, 5.46; N, 15.21.

Results and Discusson

A novel SNNS-type ligand, N,N′-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine(medpa), has been prepared from the reaction of trans-2,5-dimethylpiperazine with ethylene sulfied. Pmr spectrum of medpa (Figure 2) shows the methyl protons at 1.0 ppm as a doublet, the thiol proton at 1.6 ppm as a singlet and all the other protons ar 2.4-2.8 ppm. ^{13}C nmr spectrum of medpa (Figure 2) shows carbons in five different environments. IR spectrum of this ligand shows νSH stretching peak at 2542 cm^{-1}.

The cobalt(III) complex of medpa, $Na_4[Co_2(medpa)Cl_8]$ has been obtained from the reaction of ligand with $Na_3[Co(CO_3)_3]$ in 1 : 2 mole ratio. The νSh stretching peak has dissappeared from the ir spectrum of the complex, indicating the coordination of the surfur donor atom. In this particular complex the elemental analysis data nicely suggest whether this complex is mononuclear or binuclear complex. If the complex is mononuclear, the calculated elemental analysis values are 7.71 for N and 17.63 for S, while they are 3.86 for N and 8.84 for S in the case of a binuclear complex. The experimentally found values are 3.75 for N and 8.50 for S, which indicate that the cobalt(III) complex of medpa prepared in this work is a binuclear complex having a formula of $Na_4[Co_2(medpa)Cl_8]$ with the ligand in chair conformation. The electronic absorption spectrum of this complex (Figure 3) shows that the complex is not a mononuclear complex having either *cis* or trans geometry and that it is a sulfur coordinated

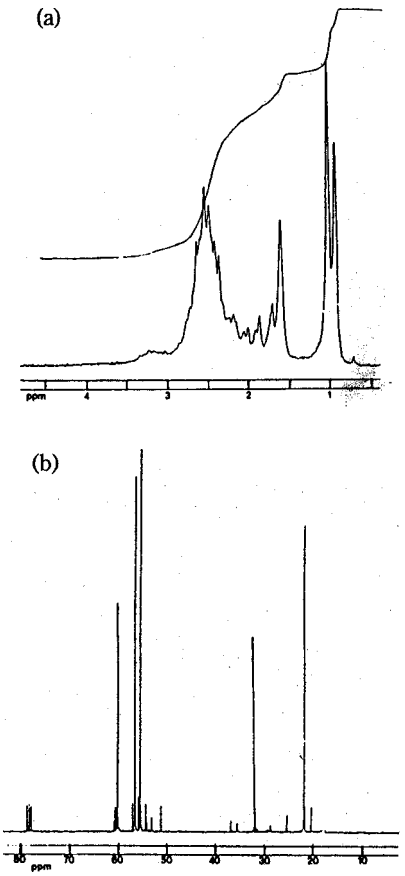


Figure 2. PMR spectrum (a) and ^{13}C NMR spectrum (b) of N,N′-bis(β-mercaptoethyl)-trans-2,5-dimethylpiperazine.

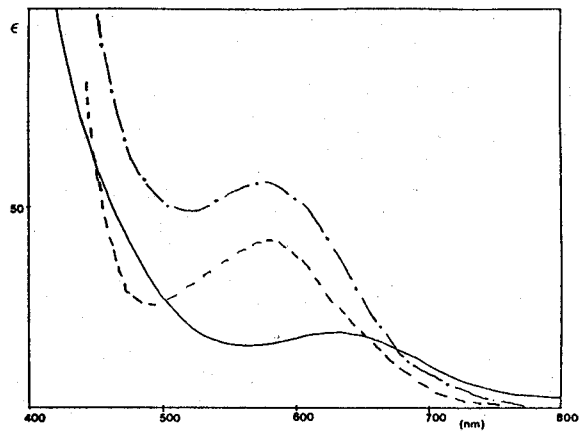


Figure 3. Electronic absorption spectra of $Na_4[Co_2(medpa)Cl_8]$ (—), $Na_4[Co_2(medpa)(NO_2)_8]$ (---), and $[Co_2(medpa)(en)_4](ClO_4)_4$ (-·-·-).

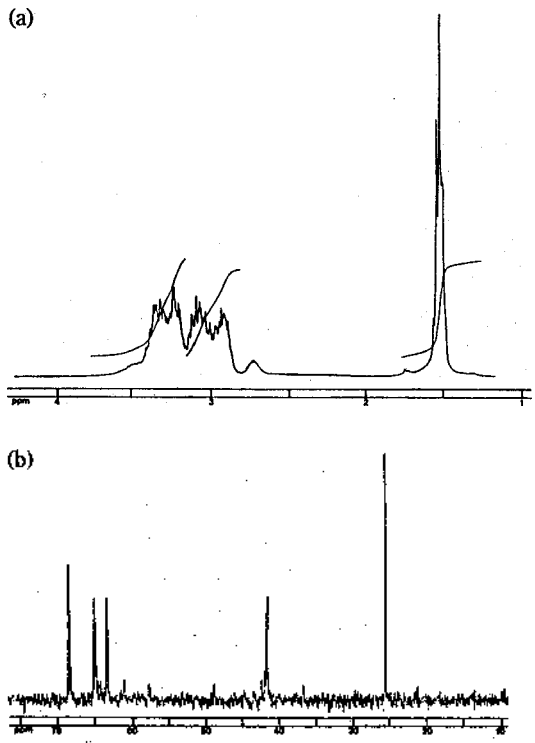


Figure 4. PMR spectrum (a) and ^{13}C NMR spectrum (b) of $Na_4[Co_2(medpa)Cl_8]$ complex.

complex having a broad d-d transition peak at 630 nm with a large S→Co charge transfer band at near 400 nm.[3~6] The pmr spectrum of this complex (Figure 4) shows the methyl protons at 1.5 ppm as a doublet, the protons between the nitrogen and sulfur donor atoms at 3.8 ppm as a doublet of doublets and the protons on the heterocyclic ring at 3.3 ppm as multiplets. The ^{13}C NMR of the complex also shows carbons in fiev different environments, which also suggest that the complex is binuclear.

The reaction of $[Co_2(medpa)Cl_8]^{4-}$ with $NaNO_2$ in 1 : 8 mole ratio has yielded the $[Co_2(medpa)(NO_2)_8]^{4-}$ complex, while the reaction of the chloro complex with en in 1 : 4 mole ratio has given the $[Co_2(medpa)(en)_4]^{4+}$ complex. Thr visible absorption spectra of these two complexes (Figure 3) show the blue shift with λ_{max} at 570 nm. The pmr spectrum of the nitro complex shows a similar pattern to the chloro complex.

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Catalytic Activity of Osmium(II) Complexes Containing Phosphine Ligands in the Homogeneous Hydrogenation of Propionaldehyde

Min-Kyo Cheong and Moo-Jin Jun*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea

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The metals in the third transition series (5*d* metals) are generally known to form very stable bonds with molecules typically involved in catalytic cycles, and are, therefore, not widely used as homogeneous catalysts.[1,2] Osmium complexes, however, can be effectively used as catalytic precursors for homogeneous hydrogenation, if the ligands of complexes and the reaction conditions are properly selected. Examples of homogeneous catalysis by the osmium complexes have so far been restricted mainly to carbonyl clusters[3] and mononuclear hydridophosphine derivatives[4].

Though homogeneous hydrogenation of C=O and C=C bonds of organic compound by ruthenium(II) complexes has been widely investigated,[5] the analogous osmium(II) complexes which are expected to have somewhat different properties are relatively less studied. We have previously reported the synthesis and catalytic activities of osmium(II) complexes containing arsine ligands for the hydrogenation of propionaldehyde.[4b,4c] Recently, we have prepared a series of new carbonyl-hydride osmium(II) complexes containing chelating phosphine ligands, $OsHCl(CO)(PPh_3)(L\text{-}L)$ [L-L=$Ph_2P(CH_2)_nPPh_2$ (n=1(**1**), 2(**2**), 3(**3**)), $Ph_2PCH=CHPPh_2$ (**4**), and $Ph_2PFe(C_5H_4\text{-}\eta^5)_2PPh_2$ (**5**)] and investigated their catalytic activities for the transfer hydrogenation of trans-cinnamaldehyde with 2-propanol as hydrogen donor.[5] We wish to report here the homogeneous hydrogenation of propionaldehyde using these osmium(II) complexes as catalysts.