Table II. Order of Conditional Stability of Methylmercury Complexes of Ligands in Aqueous Solution

pH 1:	sulfhydryl > thioether > H_2O > carboxylic acid > amine
pH 3:	sulfhydryl > thioether ~ carboxylic acid > H_2O > amine
pH 5:	sulfhydryl > carboxylic acid > thioether > amine ~ H_2O, OH^-
pH 7:	sulfhydryl > amine > OH^- > carboxylic acid > thioether
pH 9:	sulfhydryl > amine > OH^- > carboxylic acid > thioether
pH 11:	sulfhydryl > OH^- > amine > carboxylic acid > thioether

proton of methionine and the methyl protons of methylmercury for the solution containing equimolar concentrations of methylmercuric hydroxide and methionine. The procedure has been described previously.[9,14] Only data at pH values greater than 8 were used to ensure that the only complex formed was the amino complex. From the chemical shift data for the methine proton, log $K_f = 7.5 \pm 0.1$ and the chemical shift of the methine proton in the complexed form is 4.21 ppm. The chemical shift data for the methyl protons of methylmercury yielded a log K_f of 7.40 ± 0.01 and a chemical shift of 0.91 ppm for these protons when CH_3Hg^{II} is bonded to the amino group. For comparison, log K_f for the nitrogen-bonded complex of valine is 7.41 while that of the nitrogen-bonded complex of β-alanine is 7.56.[14]

The extent of complexation of methylmercury by methionine and similar molecules is strongly pH dependent due to protonation of the ligand and reaction of methylmercury with hydroxide ion. Thus the conditional formation constant, defined by eq 5, is more informative than formation constants

$$\text{methylmercury (free)} + \text{ligand (free)} \rightleftarrows \text{complex} \qquad (5)$$

of the type defined by eq 1 and 4 since the conditional formation constant indicates directly the extent of complexation for the particular set of solution conditions for which it was derived. The conditional formation constant equals $\alpha\beta K_f$, where α is the fraction of the free ligand in the form which complexes and β the fraction of free methylmercury as the aquated cation for these solution conditions. From the results reported above and elsewhere,[1,9,14] the orders of conditional stability of methylmercury complexes of sulfhydryl, amine, carboxyl, and thioether ligands have been derived as a function of pH and are given in Table II. H_2O and OH^- are included to indicate those conditions where the conditional stability constants are so small that little or no complex forms.

Because of the high degree of specificity in the binding of methylmercury by the thioether group in acidic solution, it may be possible to identify methionine resonances in the PMR spectra of methionine-containing peptides and proteins by observing changes in the spectrum as the peptide or protein is titrated with methylmercury at pH 0.5.

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Registry No. $CH_3S(HgCH_3)CH_2CH_2CH(NH_3)CO_2H$, 54517-53-2; I, 54517-54-3; methionine, 63-68-3; methylmercury$^+$, 22967-92-6.

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Contribution from the Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Japan 565

Synthesis of Novel Cationic Organonickel(II) Complexes, $[C_6Cl_5Ni(P)_{3-n}(3,5\text{-lut})_n]^+ClO_4^-$ (P = $PPhMe_2$, PPh_2Me; n = 1, 2, 3)

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In recent years the preparation, reactivity, and spectroscopic properties of a wide variety of cationic organoplatinum(II) complexes of the type $[RPt(Q)_2L]^+X^-$, where Q = tertiary phosphine or arsine and L = neutral ligand, have been investigated.[1-3] Similar studies, however, have been limited for nickel(II).[4,5] In connection with our current research program concerning the syntheses and reactions of cationic organonickel complexes, we have recently succeeded in the synthesis of the title complexes. We believe they are the first examples of cationic organonickel(II) complexes isolated with a square-planar configuration, except for the isocyanide complex reported by Cherwinski et al.[5] A cationic hydride complex has recently been reported.[6]

Results and Discussion

The chloride ligand in *trans*-$C_6Cl_5Ni(P)_2Cl$ (**1a**, P = $PPhMe_2$; **1b**, P = PPh_2Me) is labile and the complexes react readily with silver perchlorate even in a nonpolar solvent such as benzene resulting in the precipitation of silver chloride. Addition of a slight excess of 3,5-lutidine (3,5-lut) to the filtrate causes precipitation of a cationic pentachlorophenylnickel(II) complex, *trans*-$[C_6Cl_5Ni(P)_2(3,5\text{-lut})]^+ClO_4^-$, as its benzene solvate (**2'a** or **2'b**), which can be converted to the unsolvated complex (**2a** or **2b**) by recrystallization from ethanol. These complexes, **2a** and **2b**, further react with neat 3,5-lutidine giving the second type of cationic complex, *cis*-$[C_6Cl_5Ni(PPhMe_2)(3,5\text{-lut})_2]^+ClO_4^-$ (**3**), and the third type, $[C_6Cl_5Ni(3,5\text{-lut})_3]^+ClO_4^-$ (**4**), respectively (see Scheme I). In the complex **4** the pentachlorophenyl–nickel bond is still stable in the absence of tertiary phosphine ligand, which has long been known to stabilize a nickel–carbon bond.[7]

All the cationic pentachlorophenylnickel complexes thus obtained are thermally stable and each has a high melting point. They show in the ir spectra absorption bands near 1080 (vs) and 625 (s) cm^{-1}, which are characteristic of the anionic (T_d) ClO_4 group.[8] In fact the complexes **2a** and **2b** are strong electrolytes even in dichloromethane.

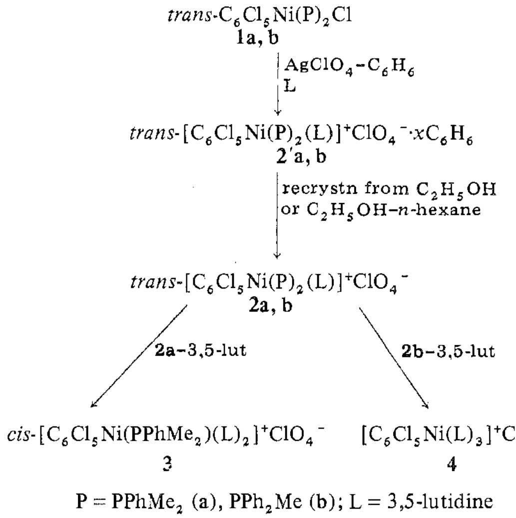
The PMR spectra of **2a** and **2b** (Table I) are consistent with diamagnetic, trans-planar structures in solution. A symmetrical 1:2:1 triplet resonance in the vicinity of τ 8–9 is assigned to the phosphine methyl protons, indicative of "virtually" coupled trans phosphines.[9] The 3,5-lutidine ligand coordinated to nickel gives singlet resonances for the 3,5-methyl and 2,6-ring protons in the spectra both of **2a** and of **2b**. Complex **3** gives a doublet resonance for the phosphine methyl protons, in accordance with

Table I. PMR Data of $[C_6Cl_5Ni(P)_{3-n}(3,5\text{-lut})_n]^+ClO_4^-$ (ppm)

Complexes			Solvent	3,5-lut			P		
No.	P	*n*	(5% w/w)	τ(3,5-CH_3)	τ(4-H)	τ(2,6-H)	τ(*P*-CH_3)	τ(*P*-C_6H_5)	*J*(PCH)[d]
2a	$PPhMe_2$	1	$CDCl_3$	7.95	*c*	2.33	8.62 t	2.6–3.1	8
2b	PPh_2Me	1	$CDCl_3$	8.04	2.96	2.14	8.17 t	2.4–2.8	7
3	$PPhMe_2$	2	$CDCl_3$	Cis[b] 7.80	*c*	1.17	8.51 d	2.6–3.0	11
				Trans[b] 7.74	*c*	1.60			
4		3	CH_2Cl_2[a]	Cis[b] 7.71	2.59	1.00			
				Trans[b] 7.69	2.52	1.32			

[a] Saturated solution (ca. 2% w/w). [b] Relative to the pentachlorophenyl group. [c] Overlapped by *P*-C_6H_5 resonance. [d] In Hz.

Scheme I



P = $PPhMe_2$ (a), PPh_2Me (b); L = 3,5-lutidine

the existence of only one phosphine coordination. An observation of two resonances for the 3,5-methyl and 2,6-ring protons of 3,5-lutidine ligands is in accordance with the existence of two kinds of ligands, and, hence, the two ligands are mutually at cis positions in this complex. In the spectra of complex **4** the methyl proton resonance of 3,5-lutidine ligands is observed at τ 7.71 with a shoulder at τ 7.69. The main resonance is attributed to the ligands situated at the cis positions to the pentachlorophenyl group, and the shoulder resonance corresponds to the trans ligand. In the same manner the stronger resonances for 2,6-ring and 4-ring protons, respectively, correspond to the cis ligands. The observation of 2,6-ring protons of *cis*-3,5-lutidines in complex **4** at lower magnetic field than that of the *trans*-lutidine is the base for the cis or trans assignment of the proton resonances for complex **3**.

Experimental Section

Both *trans*-$C_6Cl_5Ni(PPhMe_2)_2Cl$ (**1a**) and *trans*-$C_6Cl_5Ni(PPh_2Me)_2Cl$ (**1b**) were prepared by the procedure of Rausch and Tibbetts[10] and identified by PMR spectra and melting points.[10,11] Silver perchlorate and 3,5-lutidine were of commercial grade. PMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz. Chemical shifts were measured relative to TMS as an internal standard. Ir spectra were recorded on a JASCO Model IR-G spectrophotometer over the range 4000–700 cm^{-1} and on a Hitachi EPI-L spectrophotometer over the range 700–200 cm^{-1}, using Nujol mulls spread over a cesium iodide plate.

Preparation of *trans*-$[C_6Cl_5Ni(PPhMe_2)_2(3,5\text{-lut})]^+ClO_4^-$ (2a). A solution of **1a** (1.860 g, 3.00 mmol) in 25 ml of benzene was added dropwise to a solution of silver perchlorate (0.624 g, 3.01 mmol) in 35 ml of benzene. The silver chloride precipitate was removed by filtration to give an orange-brown solution, to which 3,5-lutidine (0.360 g, a slight excess) dissolved in 5 ml of benzene was added with stirring. The yellow precipitate produced at the end of the addition or by addition of 10 ml of *n*-hexane was separated by filtration, washed with *n*-hexane, and dried in air. The product yield was 2.040 g; the melting point was 130–134° when the compound was fresh and 183–185° after 4 weeks of standing in air. Elemental analyses (found: C, 47.71; H, 4.18; N, 1.85) and the PMR spectrum of the fresh product showed the existence of benzene, which was lost very slowly in air at room temperature. Recrystallization of this benzene solvate from ethanol–*n*-hexane (20:15) resulted in the formation of orange-yellow crystals of **2a** with a yield of 73%; mp 185–186°. Anal. Calcd for $NiC_{29}H_{31}NO_4P_2Cl_6$: C, 44.03; H, 3.95; N, 1.77. Found: C, 44.02; H, 4.10; N, 1.84. The ir spectrum showed the following major bands: 1600 (m), 1320 (s), 1285 (s), 1220 (m), 1080 (vs), 940 (s), 900 (s), 860 (w), 835 (w), 740 (s), 715 (w), 695 (m), 670 (w), 625 (s), 485 (s), and 415 (m) cm^{-1}. The molar conductivities of 2×10^{-3}, 2×10^{-4}, and 2×10^{-5} *M* solutions in dichloromethane were 35.3, 57.4, and 76.8 Ω^{-1} cm^2, respectively.

Preparation of *trans*-$[C_6Cl_5Ni(PPh_2Me)_2(3,5\text{-lut})]^+ClO_4^-$ (2b). Complex **2b** was obtained from a reaction between equimolar amounts of **1b** and silver perchlorate, followed by addition of 3,5-lutidine in manners similar to those of the preparation of complex **2a**. The product obtained from benzene solution had a melting point of 75–80° when it was fresh and 120–124° after 2 weeks of standing in air. Elemental analyses (found: C, 53.50; H, 4.10; N, 1.60) and the PMR spectrum of the fresh product showed the existence of benzene, which was lost very slowly in air at room temperature. Recrystallization of this benzene solvate from ethanol resulted in the formation of orange-yellow crystals of **2b** with a final yield of 75–80%; mp 203–204°. Anal. Calcd for $NiC_{39}H_{35}NO_4P_2Cl_6$: C, 51.19; H, 3.86; N, 1.53. Found: C, 51.10; H, 3.98; N, 1.69. The ir spectrum showed the following major bands: 1600 (m), 1330 (m), 1320 (m), 1290 (w), 1230 (w), 1150 (w), 1080 (vs), 885 (s), 740 (s), 695 (s), 675 (w), 636 (s), 511 (m), 477 (w), and 436 (w) cm^{-1}. The molar conductivities of 2×10^{-3}, 2×10^{-4}, and 2×10^{-5} *M* solutions in dichloromethane were 33.3, 57.0, and 74.4 Ω^{-1} cm^2, respectively.

Preparation of *cis*-$[C_6Cl_5Ni(PPhMe_2)(3,5\text{-lut})_2]^+ClO_4^-$ (3). A mixture of **2a** (0.396 g, 0.50 mmol) and 5 ml of 3,5-lutidine was heated at 100° for 5 hr. To this hot mixture was added 5 ml of ethanol and then *n*-hexane until crystals began to form (ca. 5 ml). The mixture was cooled to room temperature and placed in a refrigerator overnight. Yellow crystals were separated by filtration, washed with *n*-hexane, and dried in air to produce 0.204 g (54%) of **3**, mp 230–232°. Anal. Calcd for $NiC_{28}H_{29}N_2O_4PCl_6$: C, 44.25; H, 3.85; N, 3.69. Found: C, 44.28; H, 3.95; N, 3.87. The ir spectrum showed the following major bands: 1600 (m), 1325 (s, doublet), 1290 (s), 1150 (m), 1080 (vs), 950 (m), 910 (s), 860 (m), 740 (m), 715 (m), 695 (m), 675 (m), 625 (s), 490 (m), and 425 (w) cm^{-1}.

Preparation of $[C_6Cl_5Ni(3,5\text{-lut})_3]^+ClO_4^-$ (4). A mixture of **2b** (0.275 g, 0.30 mmol) and 5 ml of 3,5-lutidine was heated at 100° for 1 hr, during which a greenish yellow precipitate was formed. Benzene (ca. 30 ml) was added to wash the precipitate and filtered after a short period of boiling; the solid was dried in air to produce 0.200 g (91%) of **4**, mp 255° dec. Anal. Calcd for $NiC_{27}H_{27}N_3O_4Cl_6$: C, 44.49; H, 3.73; N, 5.76. Found: C, 44.29; H, 3.71; N, 5.61. The ir spectrum showed the following major bands: 1600 (m), 1330 (w), 1320 (w), 1290 (m), 1150 (m), 1090 (vs), 865 (m), 700 (m), 670 (m), and 625 (s) cm^{-1}.

Registry No. **1a**, 15526-04-2; **1b**, 26025-08-1; **2a**, 54517-11-2; **2b**, 54517-13-4; **3**, 54517-15-6; **4**, 54517-17-8.

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Synthesis and Characterization of Molybdenum(IV) and -(V) Complexes of the Cyclopentadienedithiocarboxylate Ligand

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Much of the interest which has been generated over the past few years in transition element–sulfur systems has been stimulated by the ability of sulfur-containing ligands to stabilize unusual oxidation states and to induce unusual electronic effects at the transition element center.[2–6] Yet with the exception of dithioxanthates and dithiocarbamates, relatively few sulfur-liganded complexes of molybdenum are known[7–9] even though there exist strong arguments that molybdenum–sulfur sites play important roles in molybdenum metalloenzymes.[10] In particular, no dithioaromatic or dithioaliphatic acid derivatives of molybdenum are known.

Our interest in the cyclopentadienedithiocarboxylate ligand and its unusual effect on electronic properties at metal centers[11,12] coupled with our interest in molybdenum model systems prompted the preparation and subsequent study of a tris-molybdenum(IV) and a bis-molybdenyl(V) complex.

Experimental Section

Materials. Anhydrous solvents were prepared as before.[11,12] Molybdenum tetrachloride and molybdenum oxytrichloride were obtained from Research Organic/Inorganic Chemical Corp. $(C_2H_5)_4NBr$ was obtained from Aldrich Chemical Co.

$Na_2C_5H_4CS_2 \cdot C_4H_8O$. This complex was prepared as previously reported.[8]

$[(C_2H_5)_4N]_2Mo(C_5H_4CS_2)_3$. Due to the instability of the dithiolate ligand to hydrolysis, techniques similar to those employed in the preparation of the cobalt(II) complex were used here.[12] Typically, 2.00 g of $Na_2C_5H_4CS_2 \cdot C_4H_8O$ (7.75 mm) was added to a solution of 0.609 g of $MoCl_4$ (2.58 mm) in 200 ml of *anhydrous* acetonitrile at −70°. This frozen mass was slowly warmed to room temperature while stirring and allowed to react for 1 hr at room temperature. The solution was frozen again and 1.10 g of $(C_2H_5)_4NBr$ (5.20 mm) was added. After warming to room temperature, the reaction mixture was stirred for 1 additional hr. The mixture of NaBr and NaCl which formed was removed by filtration. The volume of the reaction mixture was reduced to 50 ml and a second fraction of precipitate was collected and discarded. Further reduction of the filtrate to 30 ml produced a dark brown powder. The yield was low since a significant portion of the product precipitated in the initial volume reduction. Anal. Calcd for $[(C_2H_5)_4N]_2Mo(C_5H_4CS_2)_3$: C, 52.55; H, 6.74; N, 3.60; S, 24.75. Found: C, 52.40; H, 6.94; N, 3.84; S, 24.45.

$[(C_2H_5)_4N]MoO(C_5H_4CS_2)_2$. Synthesis was carried using an analogous procedure to that employed above except $MoOCl_3$ served as the starting material. A black (or darkly colored) precipitate was isolated from the reddish brown reaction mixture. Anal. Calcd for $[(C_2H_5)_4N]MoO(C_5H_4CS_2)_2$: C, 45.96; H, 5.40; N, 2.68; S, 24.54. Found: C, 46.10; H, 5.39; N, 2.83; S, 24.28.

Several initial attempts to synthesize this compound yielded a green oil instead of the black crystalline material. While no analyses were obtained, it is possible that insufficient precautions were taken to maintain an inert atmosphere and that a Mo(VI) complex was obtained.

Analyses. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Magnetic Susceptibility Determination. Susceptibilities were determined on solid samples at room temperature and diamagnetic corrections contributions made as before.[12]

Spectroscopic Measurements. Infrared, optical, ESR, and X-band spectra were obtained as before.[12] Second-order corrections were employed to correct for perturbations of the Zeeman transitions resulting from hyperfine interactions.[13]

Results and Discussion

The syntheses of tetraethylammonium bis(cyclopentadienedithiocarboxylato)oxomolybdenum(V) and tetraethylammonium tris(cyclopentadienedithiocarboxylato)molybdenum(IV) have been achieved.

The molybdenum(IV) complex is diamagnetic. While it is possible that some form of intermolecular interaction in the solid state might account for this diamagnetism, it is not likely.[8] The tris(1,2-dicyanoethylenedithiolato)molybdenum(IV) ion is also diamagnetic. The crystal structure of this system indicates an intermediate structure between a trigonal environment and an octahedral one at the molybdenum(IV) center.[14] Possibly in these systems (d^2), an orbitally nondegenerate level is lowest in energy. The molybdenum(V) complex also exhibits a magnetic moment characteristic of a diamagnetic complex. Since the molybdenyl complex is formally five-coordinate, it is not difficult to imagine a strong spin–spin interaction between molybdenum atoms through the sixth coordination site in the solid state. *Other monomeric MoO^{3+} systems which have magnetic moments characteristic of d^1 oxy cations are six-coordinate.*[15] The five-coordinate systems show greatly reduced susceptibilities.[16] It is also possible that in the solid the sixth site is occupied by a sulfur atom from another complex. Stacking of planar complexes of dithiolates to yield effective five- or six-coordinate complexes is known.[17]

In solution (CH_3CN) and in a frozen solution, however, the Mo(V) complex exhibits the ESR spectrum of a d^1 monomeric complex. Comparison of the intensity of this signal to that of a known $MoOCl_5^{2-}$ concentration indicates that essentially all of the Mo(V) compound is in solution. It is assumed that the sixth coordination site is occupied by a solvent molecule under these conditions. The ESR spectrum is that of a tetragonal (C_{4v}) Mo(V) complex (Figure 1). The spin hamiltonian parameters derived from this spectrum are given in Table I along with values for several other molybdenyl complexes for comparison.[18,19] Even though $g_\parallel$ and $g_\perp$ are almost perfectly coincident, it was possible to assign six of the parallel and five of the perpendicular components due to the molybdenum hyperfine splittings. The solution spectrum (Figure 2) is consistent with these assignments ($\langle a \rangle_{\text{calcd}} = {}^1/_3(A_\parallel + 2A_\perp) \simeq \langle a \rangle_{\text{obsd}}$).

The ground state for a d^1 molybdenum complex with axial symmetry is $^2B_2$ (the unpaired electron is in an antibonding molecular orbital consisting primarily of a metal d_{xy} orbital which has π symmetry in this coordinate system[20]). It is possible to evaluate certain empirical parameters of the molecular orbitals for Mo(V) complexes by the approach introduced by McGarvey using the equations[21]

$$A_\parallel = -K - 4/7\beta^2 P + (g_\parallel - 2.0023)P + 3/7(g_\perp - 2.0023)P$$

$$A_\perp = -K + 2/7\beta^2 P + 11/14(g_\perp - 2.0023)P$$

where $A_\parallel$, $A_\perp$, $g_\parallel$, and $g_\perp$ represent the hyperfine splitting parameters parallel and perpendicular to the Mo=O bond and the components of the g tensor parallel and perpendicular to the Mo=O bond, respectively. K represents the Fermi contact