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Chemistry of Molybdenum. 4.[1] Complexes of Molybdenum(VI), -(V), and -(IV) with 2-(Alkylamino)cyclopent-1-ene-1-dithiocarboxylic Acids. Synthesis, Electrochemistry, and Spectroscopic Properties

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This article reports the synthesis, spectra, electrochemistry, and magnetic behavior of a number of molybdenum(VI), -(V), and -(IV) compounds with 2-(alkylamino)cyclopent-1-ene-1-dithiocarboxylic acids (HL-R: R = Et, *n*-Pr, *n*-Bu, *n*-Hx) as the $(S,S)^-$ donor metal binding substrates. The Mo(VI) compounds are either *cis*-dioxo, $MoO_2(L\text{-}R)_2$, or seven-coordinated dichloro, $MoOCl_2(L\text{-}R)_2$, species. The monooxo Mo(V), $MoO(L\text{-}R)_2(L\text{-}H)$, and non-oxo Mo(IV), $Mo(L\text{-}R)_2(L\text{-}H)_2$, compounds are derived from $MoO_2(L\text{-}R)_2$ and $MoOCl_2(L\text{-}R)_2$, respectively, by oxo-abstraction reactions using 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (HL-H) as the redox-coordinating agent. Gradual depletion of oxygen atom(s) from the oxomolybdenum center on going from *cis*-$Mo^{VI}O_2$ to Mo(IV) is clearly seen in their IR spectra. Mo(V) compounds are monomeric ($\mu_{eff} \approx 1.60\ \mu_B$) and their EPR spectral features show substantial metal character in the ground state. Magnetic behavior of the Mo(IV) compounds probably provides the first reported example of a series of compounds containing an MoS_8 core having a spin triplet ground state (μ_{eff} = 2.35–2.77 μ_B). Electrochemical properties of some of these compounds are examined by cyclic voltammetry, differential pulse voltammetry, and coulometry. Cyclic voltammograms of $MoO_2(L\text{-}R)_2$ complexes are typically irreversible, involving Mo(VI)–Mo(V) single-electron transfer ($E_{irr} \approx -0.90$ V vs. SCE). $MoOCl_2(L\text{-}R)_2$ compounds undergo quasi-reversible reduction ($E_{1/2} \approx -0.20$ V). The voltammetric behaviors of all of the Mo(IV) complexes except $Mo(L\text{-}Bu)_2(L\text{-}H)_2$ are almost identical, involving both reversible one-electron-reduction ($E_{1/2} \approx -0.40$ V) and -oxidation waves ($E_{1/2} \approx -0.20$ V). For $Mo(L\text{-}Bu)_2(L\text{-}H)_2$ the oxidation process is a two-electron phenomenon involving Mo(VI)–Mo(IV) electron transfer.

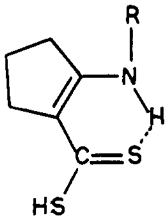
Introduction

The chemistry of sulfur-rich molybdenum compounds has become the subject of intensive research because of their close relevance to molybdoenzymes. Recent spectroscopic and EXAFS studies have delineated the metal binding sites of these enzymes[2-5] and have indicated that, in their biological functions, the oxidation state of molybdenum cycles between +6 and +4 during substrate binding and reactivation.[6] We, for some time, have been interested in investigating structure–redox activity correlations of molybdenum compounds with varying degrees of sulfur coordination[1,7,8] and have noted that the oxygen atoms of the oxomolybdenum species play a significant role in the nature of electrode processes. It appears[1,8,9] that the kinetics of electron transfer become increasingly sluggish as more oxygen atoms are bound to the metal center. However, to get a clearer insight and to establish this rationale, a useful strategy would be to synthesize and investigate redox behavior of molybdenum compounds that are successively depleted of oxygen atoms.

Here we report the synthesis, electronic, IR, and EPR spectra, and electrochemistry of a number of molybdenum compounds containing the $Mo^{VI}O_2(S,S)_2$, $Mo^{VI}OCl_2(S,S)_2$, $Mo^{V}O(S,S)_3$, and $Mo^{IV}(S,S)_4$ cores in which oxygen atoms are sequentially removed from the oxomolybdenum center by oxygen abstraction reactions utilizing 2-(alkylamino)cyclopent-1-ene-1-dithiocarboxylic acid (1) as the $(S,S)^-$ donor metal binding substrate.

Experimental Section

Physical Measurements. IR spectra were obtained as KBr pellets on a Perkin-Elmer 783 spectrometer and UV–visible spectra on a Pye-Unicam Model SP8-150 spectrometer. Bulk magnetic susceptibilities at room temperature were measured with a PAR 155 vibrating-sample magnetometer and solution electrical conductivity with a Philips PR 9500 bridge. Room-temperature EPR spectra of the compounds in powdered form as well as in solution (1:10 v/v DMF–$CHCl_3$) were recorded at X-band frequency on a Varian E-109 spectrometer equipped with a 100-kHz field modulation unit. Cyclic voltammetry and differential pulse voltammetry were performed under a dinitrogen atmosphere with the help of a PAR Model 370-4 electrochemistry system having among other things a 174A polarographic analyzer, a 175 universal programmer, and a RE 0074 X-Y recorder. In the three-electrode configuration either a Beckman Model 39273 platinum electrode or a Metrohm E410 hanging-mercury-drop electrode (HMDE) was the working electrode. For controlled-potential coulometry a Model 173 potentiostat, 179 digital coulometer, and 377A cell system having a mercury-pool electrode was used. All measurements were made at 298 K. The potentials are referenced to the saturated calomel electrode (SCE) and are uncorrected for junction contribution.



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R = H: HL-H
R = C_2H_5: HL-Et
R = *n*-C_3H_7: HL-Pr
R = *n*-C_4H_9: HL-Bu
R = *n*-C_6H_{13}: HL-Hx

Materials. Reagent grade solvents, distilled and dried by standard methods, were used in all cases. Reactions and manipulations of compounds involving Mo(V) and Mo(IV) were carried out under purified dinitrogen. *n*-Propylamine, *n*-butylamine, and *n*-hexylamine were of >99% purity (K. Light) and distilled over KOH prior to use. All other chemicals used for preparative work were of reagent grade and employed without further purification. $MoO_2(acac)_2$ (acac = acetylacetonate anion) was prepared by a known method.[10]

Ligands. The ligands 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (HL-H), 2-(ethylamino)cyclopent-1-ene-1-dithiocarboxylic acid (HL-Et), and 2-(butylamino)cyclopent-1-ene-1-dithiocarboxylic acid (HL-Bu) were prepared as described earlier.[8] 2-(Propylamino)cyclopent-1-ene-1-dithiocarboxylic acid (HL-Pr) was obtained as a yellow crystalline solid (mp 142 °C) from the reaction of *n*-propylamine and HL-H by the

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Table II. IR Data (cm^{-1}) and Tentative Band Assignments for the Complexes

complex	ν(Mo=O)	ν_{asym}(CSS)	ν(Mo—S)	ν(Mo—Cl)
$MoO_2(L-Pr)_2$	935 (vs), 895 (vs)	830 (s)	390 (s)	
$MoO_2(L-Hx)_2$	930 (vs), 895 (vs)	830 (s)	390 (s)	
$MoOCl_2(L-Et)_2$	950 (vs) 915 (vs)[a]	835 (s)	380 (s)	310 (w)
$MoOCl_2(L-Pr)_2$	950 (vs) 920 (vs)[a]	830 (s)	385 (s)	315 (w)
$MoOCl_2(L-Bu)_2$	950 (vs) 920 (vs)[a]	835 (s)	375 (s)	310 (m)
$MoOCl_2(L-Hx)_2$	940 (vs) 920 (vs)[a]	825 (s)	380 (s)	310 (w)
$MoO(L-Et)_2(L-H)$	945 (s)	830 (s)	385 (m)	
$MoO(L-Pr)_2(L-H)$	955 (s)	810 (s)	350 (m)	
$MoO(L-Bu)_2(L-H)$	945 (s)	810 (s)	365 (m)	
$MoO(L-Hx)_2(L-H)$	960 (s)	830 (s)	370 (m)	
$Mo(L-Et)_2(L-H)_2$		810 (s)	345 (m), 330 (m)	
$Mo(L-Pr)_2(L-H)_2$		815 (s)	345 (m), 330 (m)	
$Mo(L-Bu)_2(L-H)_2$		815 (s)	350 (m)	
$Mo(L-Hx)_2(L-H)_2$		815 (s)	350 (m), 330 (m)	

[a] Measured in dichloromethane solution.

method of Bordas et al.[11] 2-(*n*-Hexylamino)cyclopent-1-ene-1-dithiocarboxylic acid (HL-Hx) was synthesized with the use of a slight modification of a published procedure[11] by dropwise addition of freshly distilled *n*-hexylamine (15 g, 0.15 mol) with stirring to HL-H (6.36 g, 0.04 mol) in methanol (60 mL) and reflux of the solution for 6 h. The dark red solution was cooled to room temperature, 200 mL of a water–ethanol (1:2 v/v) mixture was added to it, and the solution was filtered. The yellow filtrate, slightly turbid in nature, was neutralized with 2 M HCl under ice cooling, and the precipitated yellow product was collected by filtration, washed with water, and dried. The crude product was recrystallized from acetone: mp 145 °C; yield 3.9 g (40%).

Complexes. $MoO_2(L-Pr)_2$ (2a). A cold (5 °C) filtered solution of 0.8 g (4.0 mmol) of HL-Pr in acetone (30 mL) was added slowly with stirring to a cold (5 °C) methanol solution (50 mL) of $MoO_2(acac)_2$ (0.66 g, 2.0 mmol). The solution immediately turned deep red, from which beautiful cherry red shining crystals deposited slowly. The product was collected by filtration, washed with acetone (4 × 10 mL), and finally dried in vacuo; yield 75%.

$MoO_2(L-Hx)_2$ (**2b**) was prepared similarly with an yield of 60%.

$MoOCl_2(L-Pr)_2$ (3b). To a stirred suspension of 0.27 g (0.5 mmol) of $MoO_2(L-Pr)_2$ in 30 mL of dioxane was added dropwise 2.5 mL of 1.8 M HCl (in dioxane) over a period of 30 min. The suspension was stirred at room temperature for 7 h, when the color of the reaction mixture faded from its original cherry red. The saffron-colored microcrystalline product was separated by filtration, washed with $CHCl_3$ (3 × 10 mL), and dried in vacuo; yield 54%.

$MoOCl_2(L-Et)_2$ (**3a**), $MoOCl_2(L-Bu)_2$ (**3c**), and $MoOCl_2(L-Hx)_2$ (**3d**) were obtained by following the same procedure as mentioned above in yields of 40–50%.

$MoO(L-Pr)_2(L-H)$ (4b). In a three-necked flask equipped with a reflux condenser and a dropping funnel was suspended 0.27 g (0.5 mmol) of $MoO_2(L-Pr)_2$ in 30 mL of methanol. The suspension was stirred magnetically under dinitrogen, and a solution of 0.18 g of HL-H (1.1 mmol) in 20 mL of methanol was added to it over a period of 45 min. The resulting solution was warmed to 40 °C, and the stirring was continued for 4 h. During this period the color of the mixture changed from red to black through an intermediate red-brown stage. After the mixture was cooled, the black microcrystalline product was filtered, washed with a chloroform–hexane (1:2 v/v) mixture (4 × 10 mL), and finally dried in vacuo. The purity of the product was checked by TLC; yield 70%.

The remaining $MoO(L-R)_2(L-H)$ complexes with other substituents (R = C_2H_5 (**4a**), *n*-C_4H_9 (**4c**), *n*-C_6H_{13} (**4d**)) were prepared similarly; yield 50–65%.

$Mo(L-Pr)_2(L-H)_2$ (5b). In a three-necked flask fitted with a reflux condenser and a dropping funnel was suspended finely ground $MoOCl_2(L-Pr)_2$ (0.29 g, 0.5 mmol) in 30 mL of methanol. The stirred suspension was warmed to 40 °C, and a solution of HL-H (0.35 g, 2.2 mmol) in methanol (40 mL) was added dropwise over a period of 45 min under dinitrogen. At the end of the addition, the stirring was continued for an additional 4 h. The solution was then cooled to room temperature, and the black-violet product formed was filtered, washed with a 1:3 v/v chloroform–hexane mixture, and finally dried in vacuo. The purity of the product was checked by TLC; yield 70%.

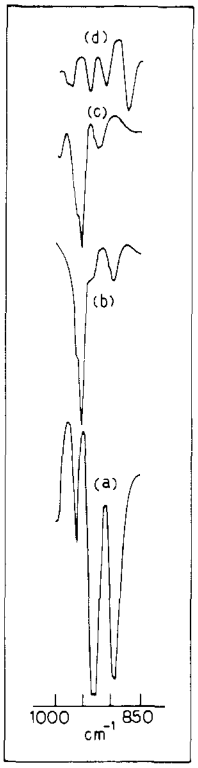

Figure 1. IR spectra of (a) $MoO_2(L-Pr)_2$, (b) $MoOCl_2(L-Pr)_2$, (c) $MoO(L-Pr)_2(L-H)$, and (d) $Mo(L-Pr)_2(L-H)_2$ showing gradual abstraction of oxygen atoms from the oxomolybdenum center.

The complexes with other substituents (R) can be synthesized similarly with varying yields (55–70%).

The compounds reported are sufficiently pure and gave satisfactory analytical results (Table I, supplementary material).

Results and Discussion

A. $MoO_2(L-R)_2$ (2a,b) and $MoOCl_2(L-R)_2$ (3a–d) Complexes.

$MoO_2(L-R)_2$ (R = *n*-C_3H_7, *n*-C_6H_{13}) compounds are formed according to the reaction

$$MoO_2(acac)_2 + 2HL\text{-}R \rightarrow MoO_2(L\text{-}R)_2 + 2Hacac$$

Infrared spectra of these complexes (Table II, Figure 1) in the range 1000–850 cm^{-1} display a strong two-band pattern characteristic of a *cis*-dioxomolybdenum(VI) center.[12] The (S,S) mode of the metal–ligand binding in these compounds has also been established from infrared spectra.[1,8] Their IR spectra contain a single sharp carbon–sulfur stretching in the ~830-cm^{-1} region

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Table III. Summary of Electronic Spectral[a] and Electrochemical[b] Data for $MoO_2(L-R)_2$ Complexes

		Mo(VI)/Mo(V)	
complex	λ_{max}/nm (ϵ_{max}/mol^{-1} cm^2)	$(E_{irr})_1{}^c$/V	$n_{irr}{}^d$
$MoO_2(L-Pr)_2$	458 (22 800), 380 (31 50), 296 (13 300)	−0.89	0.95
$MoO_2(L-Hx)_2$	458 (20 400), 382 (30 300), 298 (12 900)	−0.93	0.92

[a] In dichloromethane solution. [b] Conditions: solvent DMF; supporting electrolyte TEAP (0.1 M); solute concentration $\sim 10^{-3}$ M. [c] Calculated from DPV data: scan rate 5 mV s^{-1}; modulation amplitude (ΔE) 10 mV; $(E_{irr})_1 = E_{pc} + 0.5(\Delta E)$, where E_{pc} is DPV peak potential. [d] Number of electrons per molecule determined by comparison of voltammetric peak current parameters (see text).

due to ν_{asym}(CSS) with no evidence for splitting, indicating that (L-R)$^-$ ligands are bidentate.[13] The synthesis and characterization of other $MoO_2(L-R)_2$ (R = H, C_2H_5, n-C_4H_9) complexes have been reported elsewhere.[8]

$MoOCl_2(L-R)_2$ (**3a–d**) compounds are obtained as orange microcrystalline solids by reacting a suspension of $MoO_2(L-R)_2$ in dioxane with 2 equiv of HCl:

$$MoO_2(L\text{-}R)_2 + 2HCl \rightarrow MoOCl_2(L\text{-}R)_2 + H_2O$$

These compounds are stable in the solid state, and conductivity measurements show that they are nonelectrolytes in dichloromethane solution, thus suggesting a seven-coordinated geometry around the metal center as reported for similar dithiocarbamato complexes.[14] Since the oxygen atoms of the *cis*-dioxo compounds are highly basic due to a strong π-bonding interaction of the sulfur atoms,[15,16] an initial protonation on the electron-rich oxygen atom followed by chloride ion inclusion in the metal coordination sphere are assumed to be the two consecutive steps involved in the actual reaction pathway.[17]

In addition to the strong band at ~830 cm^{-1} due to asymmetric CSS stretching the IR spectra of the $MoOCl_2(L-R)_2$ complexes are characterized by a strong band attributed to ν(Mo=O)[14–17] but shifted to higher frequencies, ~950 cm^{-1}, than those observed for parent *cis*-O_2 Mo^{VI} compounds due to the greater availability of the metal dπ orbitals for bond formation.[18] Their spectra also contain a weak band in the ~310-cm^{-1} region assignable to ν(Mo—Cl).[19]

Electronic absorption spectra of the $MoO_2(L-R)_2$ complexes in dichloromethane solution contain several absorption maxima in the range 600–250 nm (Table III, Figure 2). The absorption bands appearing below 400 nm are due to internal ligand transitions.[8,20] The lowest energy band displayed by the compounds at ~460 nm is assignable to a ligand-to-metal charge transfer (LMCT) originating from an electronic excitation from the highest occupied ligand molecular orbital to the lowest unoccupied metal orbital.

The electronic spectral features of various $MoOCl_2(L-R)_2$ type complexes measured both in solution (dichloromethane) and in the solid state (Nujol mull) are given in Table IV (Figure 2). Of particular interest to us is the energy of the LMCT band, S(π) → Mo(dπ), which is significantly shifted to higher energy when measured in solution (λ_{max} 450 nm), compared to that in the solid state (λ_{max} 490 nm), thus suggesting a conformational change in the Mo site symmetry in solution and in the solid state. IR spectra of the $MoOCl_2(L-R)_2$ compounds when measured in dichloromethane solution (Table II) show a lower frequency shift of the ν(Mo=O) stretching vibration, indicating a low Mo–O π-bond order in solution compared to that in the solid state. The existence of similar differences in Mo–O π-bond order in solution and in the solid state for a pair of analogous dithiocarbamato complexes, viz., $MoOX_2(Et_2dtc)_2$ (X = Cl, Br; Et_2dtc^- = diethyldithiocarbamato anion) has also been confirmed by X-ray structure determination,[14] IR, and ^{17}O NMR studies.[17]

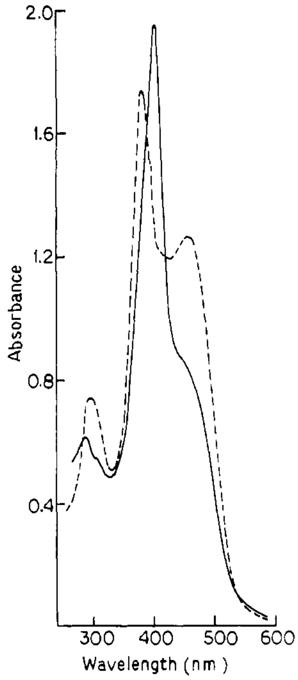

Figure 2. Electronic spectra of $MoO_2(L-Pr)_2$ (5.47×10^{-5} M) (---) and $MoOCl_2(L-Pr)_2$ (4.92×10^{-5} M) (—) in CH_2Cl_2 solution.

The electron-transfer behavior of Mo(VI) complexes (**2a,b**, **3a–d**) was examined in DMF (0.1 M TEAP) at a platinum or a hanging-mercury-drop electrode (HMDE) with use of cyclic voltammetric and differential pulse voltammetric techniques. For both the $MoO_2(L-R)_2$ complexes reported here (Table III) we observe a well-defined cathodic response with a peak potential (E_{pc}) of ~−0.90 V. No detectable oxidation wave was seen in the voltammograms during reverse anodic scans even at a high scan rate (500 mV s^{-1}). Evidently the reduced product is unstable in the voltammetric time scale studied (up to 500 mV s^{-1}) and does not survive to undergo reoxidation. Coulometry at potentials more negative than E_{pc} did not give meaningful results due to continuous accumulation of coulombs arising from unidentified reaction(s). However, by comparison of the cathodic peak current with those of authentic one-electron reversible reactions measured under identical experimental conditions,[1,21,22] the reduction peaks observed for $MoO_2(L-R)_2$ are found to involve only one electron. On the basis of electrochemical results, we propose the general reactions (1) for the $MoO_2(L-R)_2$ complexes. It must be emphasized that the $(E_{irr})_1$ values reported here (Table III) are not true reduction potentials but are calculated from differential pulse voltammetric data by utilizing the equation[23]

$$Mo^{VI}O_2(L\text{-}R)_2 + e^- \xrightarrow{(E_{irr})_1} Mo^{V}O_2(L\text{-}R)_2^- \xrightarrow{\text{fast}} \text{decomposition product(s)} \quad (1)$$

$$E_{irr} = E_{pc} + \Delta E/2$$

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Table IV. Summary of Electronic Spectral and Electrochemical Data for $MoOCl_2(L{-}R)_2$ Complexes

	λ_{max}/nm (ϵ/mol^{-1} cm^2)		Mo(VI)/Mo(V)[c]			
complex	soln[a]	powdered solid[b]	$(E_{1/2})_2$/V[d]	ΔE_p/mV[e]	i_{pc}/i_{pa}	n[f]
$MoOCl_2(L{-}Et)_2$	452 (sh), 400 (40 500), 312 (sh), 292 (12 300)	480, 408	−0.21	100	0.95	0.96
$MoOCl_2(L{-}Pr)_2$	452 (sh), 400 (39 500), 312 (sh), 286 (12 200)	485, 405	−0.20	90	1.15	0.91
$MoOCl_2(L{-}Bu)_2$	452 (sh), 400 (42 200), 312 (sh), 285 (13 000)	495, 408	−0.20	90	0.97	1.10
$MoOCl_2(L{-}Hx)_2$	460 (sh), 400 (38 700), 312 (sh), 292 (11 700)	490, 400	−0.22	100	0.85	0.95

[a] Spectra were taken in CH_2Cl_2 solution. [b] In Nujol mull. [c] Conditions: solvent DMF; supporting electrolyte TEAP (0.1 M); solute concentration ~10^{-3} M. [d] From CV using a scan rate of 50 mV s^{-1}: $(E_{1/2})_2 = 0.5(E_{pc} + E_{pa})$. [e] $\Delta E_p = E_{pc} - E_{pa}$. [f] Number of electrons per molecule determined by controlled-potential coulometry.

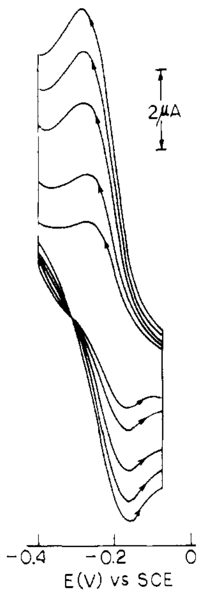

Figure 3. Cyclic voltammetric traces for ~1 × 10^{-3} M $MoOCl_2(L\text{-}Hx)_2$ in 0.1 M TEAP/DMF (scan rates 50, 100, 200, 300, and 400 mV s^{-1}).

where E_{pc} is the cathodic peak potential and ΔE is the modulation amplitude.

Although irreversibility in electron-transfer behavior is almost a common phenomenon for a *cis*-O_2Mo^{VI} center,[24-26] the electrochemical behavior of the $MoOCl_2(L\text{-}R)_2$ complexes is quite interesting in the sense that it offers a rare example[27] where a Mo(VI) compound undergos a quasi-reversible electron transfer. Figure 3[28] shows the voltammetric features of $MoOCl_2(L\text{-}Hx)_2$ at several scan rates (v). As shown in the figure, the cathodic peak height increases in proportion to $v^{1/2}$ and E_{pc} becomes more negative as v increases, showing that the reduction process is quasi-reversible in the electrochemical sense. From electron stoichiometry determination by controlled-potential coulometry (CPC) at a potential ~200 mV more negative than E_{pc}, reaction 2 is judged to be a quasi-reversible metal-centered one-electron

$$Mo^{VI}OCl_2(L\text{-}R)_2 + e^- \overset{(E_{1/2})_2}{\rightleftharpoons} Mo^{V}OCl_2(L\text{-}R)_2^- \quad (2)$$

transfer comprising the Mo(VI) and Mo(V) oxidation states. One interesting observation (Table IV) is the large positive shift (~700 mV) in $E_{1/2}$ values when one of the oxygen atoms of the *cis*-dioxomolybdenum is replaced by two chlorine atoms in $MoOCl_2(L\text{-}R)_2$. The reason for this is the substantial drainage of electronic charge density from the central metal ion to the more electronegative coordinated chloride ions. This in turn results in an appreciable increase in the formal positive charge on the central metal ion and thus favors an easier reduction.

Table V. Electronic Spectral, Magnetic, and EPR Data for the $MoO(L{-}R)_2(L{-}H)$ Complexes

compd	λ_{max}/nm (ϵ/mol^{-1} cm^2)[a]	μ_{eff}, μ_B	$\langle g\rangle$[b]	$10^4\langle A\rangle$/cm^{-1}
$MoO(L{-}Et)_2(L{-}H)$	808 (1150), 652 (2500), 538 (sh), 380 (29 500), 336 (18 100)	1.54	1.986	31.1
$MoO(L{-}Pr)_2(L{-}H)$	812 (1050), 648 (2360), 538 (sh), 382 (29 800), 338 (15 500)	1.69	1.984	31.5
$MoO(L{-}Bu)_2(L{-}H)$	808 (1250), 652 (2530), 538 (sh), 382 (29 400), 336 (17 000)	1.58	1.984	31.5
$MoO(L{-}Hx)_2(L{-}H)$	813 (1330), 656 (2670), 540 (sh), 386 (38 600), 338 (18 400)	1.60	1.985	32.00

[a] Spectra were recorded in DMF solution. [b] In 10:1 chloroform–DMF mixture at room temperature.

B. $MoO(L\text{-}R)_2(L\text{-}H)$ (4a–d) Complexes. With use of the ability of 2-aminocyclopent-1-ene-1-dithiocarboxylic acid (HL-H) to reduce molybdenum–oxo species, various Mo(V) complexes of the type $MoO(L\text{-}R)_2(L\text{-}H)$ (**4a–d**) have been synthesized by the direct reaction of $MoO_2(L\text{-}R)_2$ with excess HL-H (1:2 mole ratio) in methanol. A similar synthetic route has been successfully used earlier[29] to obtain Mo(V) compounds from MoO_2Cl_2 using the sodium salt of thiobenzoic acid as the redox-coordinating agent. The $MoO(L\text{-}R)_2(L\text{-}H)$ compounds, which are air stable in the solid state but are slowly oxidized in solution, are formulated on the basis of elemental analysis and a variety of physical measurements.

The spectral characterization data (Table V) for $MoO(L\text{-}R)_2(L\text{-}H)$ complexes are relatively straightforward. Infrared spectra of the compounds show a strong band at 830–810 cm^{-1} characteristic of the $(S,S)^-$ mode of chelation by the ligands. A strong band appearing at ~950 cm^{-1} (Figure 1) can be assigned to the Mo–axial oxygen bond.[30] The strong terminal axial oxygen band and the absence of bands for Mo–O–Mo bridge vibrations

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(28) The cyclic voltammograms of a representative member, viz., $MoOCl_2(L\text{-}Hx)_2$, is shown in Figure 3 at several scan rates (v). Similar voltammograms are also observed with **3a**, **3b**, and **3c** in this region.

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(30) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

Table VI. Electronic Spectral, Magnetic, and Electrochemical Data for $Mo(L-R)_2(L-H)_2$ Complexes

			Mo(IV)/Mo(III)[b]				Mo(IV)/Mo(V),Mo(VI)[b]		
compd	λ_{max}/nm[a] (ϵ/mol^{-1} cm^2)	μ_{eff}, μ_B	$(E_{1/2})_3$/V[c]	ΔE_p/mV[d]	i_{pc}/i_{pa}	n[e]	$(E_{1/2})_4$/V[c]	ΔE_p/mV[d]	i_{pc}/i_{pa}
$Mo(L-Et)_2(L-H)_2$	808 (2220), 744 (sh), 656 (4800), 536 (10 300), 454 (sh), 382 (37 100)	2.46	−0.42	70	1.0	1.05	−0.20	90	1.0
$Mo(L-Pr)_2(L-H)_2$	808 (2700), 746 (sh), 660 (6200), 540 (13 300), 495 (13 000), 382 (42 000)	2.50	−0.42	70	0.95	0.98	−0.20	80	1.0
$Mo(L-Bu)_2(L-H)_2$	808 (2800), 744 (sh), 662 (6800), 540 (14 500), 496 (10 100), 386 (42 000)	2.35	−0.42	60	0.90	1.10	−0.21	80	0.95
$Mo(L-Hx)_2(L-H)_2$	804 (2800), 740 (sh), 658 (6100), 534 (13 250), 496 (13 500), 387 (45 500)	2.77	−0.46	140	0.90	0.95	−0.19	160	1.1

[a] Spectra were recorded in DMF solution. [b] Cyclic voltammograms performed in 0.1 M TEAP/DMF with $\sim 10^{-3}$ M compound at a HMDE working electrode. [c] Potentials are vs. SCE and are estimated from cyclic voltammetry with a scan rate of 50 mV s^{-1}: $E_{1/2} = 0.5(E_{pc} + E_{pa})$. [d] $\Delta E_p = E_{pc} - E_{pa}$. [e] Number of electrons per molecule determined from controlled-potential coulometry.

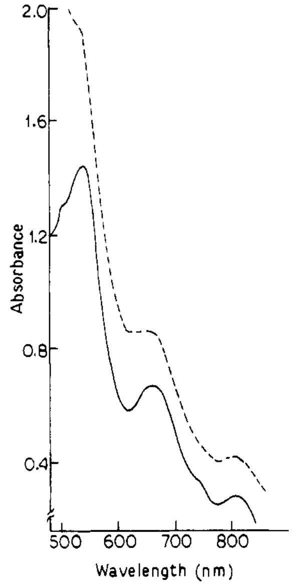

Figure 4. Electronic spectra of $MoO(L-Bu)_2(L-H)$ (3.4×10^{-5} M) (---) and $Mo(L-Bu)_2(L-H)_2$ (2.96×10^{-5} M) (—) in DMF solution.

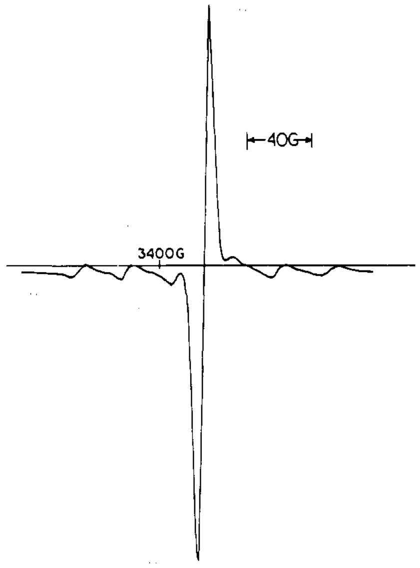

Figure 5. X-Band EPR spectrum at room temperature of $MoO(L-Bu)_2(L-H)$ in 1:10 v/v DMF–$CHCl_3$ solution (10^{-3} M). The satellites belong to odd isotopes of molybdenum.

indicate a monomeric nature of the Mo(V) compounds.

The electronic spectral data of these complexes (Figure 4)[31] are summarized in Table V. The band positions are fairly close to those[1] reported for other similar monomeric Mo(V) complexes. All bands appearing below 400 nm are due to intraligand transitions. The results are consistent with the $(4d_{xy})^1$ electronic ground state ($^2B_2$) for Mo(V). While bands at ~810 and ~540 nm ar assigned to $^2B_2 \rightarrow {}^2E$ ($O_{2p_\pi} \rightarrow Mo_{4d_{xy}}$) and $^2B_2 \rightarrow {}^2E$ ($Mo_{4d_{xy}} \rightarrow Mo_{4d_{xz,yz}}$) electronic transitions, respectively,[32] the corresponding band at ~650 nm may be tentatively assigned to a ligand-to-metal (S → Mo) charge transfer.[33]

The magnetic moment and EPR data for the Mo(V) complexes are listed in Table V. The compounds are formally d^1 with the magnetic moments ($\mu_{eff} \approx 1.60\ \mu_B$) much closer to the spin-only value, indicating that the orbital angular momentum is effectively quenched by the low symmetry of the ligand field surrounding the central metal ion. Figure 5 shows the X-band isotropic solution (1:10 v/v DMF–$CHCl_3$) EPR spectrum of $MoO(L-Bu)_2(L-H)$, which contains a strong central line due to the 75% Mo isotopes with $I = 0$ and six satellite lines arising from the hyperfine interaction of the unpaired electron with ^{95,97}Mo nuclei of spin $^5/_2$. Similar spectra were also obtained for the other remaining Mo(V) complexes (**4a,b,d**). The isotropic $\langle g \rangle$ and $\langle A \rangle$ values (Table V) obtained are almost identical, virtually independent of the ligand substituents, thus suggesting substantial metal character in the ground state of the complexes. Of particular interest are the tabulated values of $\langle g \rangle$ and $\langle A \rangle$, which reveal some interesting trends when compared with those of other Mo(V) complexes with different donor atom sets.[34] All the OMo(V) complexes reported here contain six coordinated S atoms and display $\langle g \rangle$ values somewhat higher and $\langle A \rangle$ values significantly lower than those of many reported Mo(V) complexes.[34] This, however, is in complete agreement with previous reports,[35,36] where an increase in $\langle g \rangle$ values and a concomitant decreases in $\langle A \rangle$ values are observed with increasing number of sulfur atoms ligated to the metal center.

C. $Mo(L-R)_2(L-H)_2$ (5a–d) Complexes. The reaction between $MoOCl_2(L-R)_2$ compounds and excess HL-H (1:4 mole ratio) in methanol under a dinitrogen atmosphere results in the formation of the new black-violet dichroic compounds $Mo(L-R)_2(L-H)_2$. The preparation described here is unique in the sense that this is probably one of the rare examples of the synthesis of non-oxo eight-coordinated Mo(IV) compounds where both reduction and oxo abstraction have been simultaneously achieved with the same coordinating ligand. This, according to our speculation, is made possible because of the presence of two strongly electron-withdrawing chloride ions, which remove the π density from the Mo=O unit to such an extent that the Mo=O bond becomes extremely labile to facilitate smooth oxo abstraction. A similar reduction and deoxygenation mechanism has recently been proposed[37] for the synthesis of $Mo(pdc)_4$ (pdc = pyrrole-*N*-carbo-

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(31) The electronic spectrum of $MoO(L-Bu)_2(L-H)$ is shown as a typical one. The gross features of the electronic spectra of the remaining compounds (**3a**, **3b**, and **3d**) are similar.

(32) (a) Garner, C. D.; Hiller, I. H.; Mabbs, F. E. *Chem. Phys. Lett.* **1975**, *32*, 224. (b) Allen, E. A.; Brisdon, B. J.; Edwards, D. A.; Fowles, G. W. A.; Williams, R. G. *J. Chem. Soc.* **1963**, 4649.

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dithioate) from an aqueous MoO^{3+} core. All other reported methods[38–41] for the generation of compounds of the type $Mo^{IV}L_4$ involve the use of non-oxo molybdenum starting materials.

Infrared spectra of the Mo(IV) complexes are very similar to the spectral nature of other compounds as documented in Table II except in the region 1000–850 cm^{-1} (Figure 1), where the absence of characteristic bands suggests complete removal of the oxo group from the coordination sphere. The electronic spectra of the Mo(IV) compounds are reported in Table VI and Figure 4.[42] The spectral nature is very similar to that of other reported eight-coordinated Mo(IV) (d^2) systems containing (MoS_8) chromophores.[37,38,43,44] In addition to the high-energy π–π^* internal ligand transitions, five more bands, each associated with high intensity, are observed in the region 450–850 nm for these compounds in DMF solution. A change in alkyl substitution in the ligand framework appears to have very little influence on the spectroscopically accessible energy levels of $Mo(L\text{-}R)_2(L\text{-}H)_2$ compounds. While no attempt has been made to interpret these complicated spectra, however, it would be reasonable to comment that on the basis of high molar extinction values (2000–14 500 mol^{-1} cm^2) these transitions are probably a L $\rightarrow$ M charge-transfer type.

The room-temperature magnetic data of the Mo(IV) complexes (Table VI) probably indicate a d^2 spin triplet ground state. To date, barring a few scattered examples,[39,40] most of the reported eight-coordinated Mo(IV) complexes are found to be diamagnetic.[37,38,43,44] Diamagnetism in these complexes is explained on the basis of their dodecahedral (D_{2d}) or square-antiprismatic (D_{4d}) geometries. In these configurations the $d_{x^2-y^2}$ or d_{z^2} metal orbitals are sufficiently energetically low lying to accommodate the electron pair to provide a spin-paired ground state.[38] Although this explanation has its general validity for monodentate ligands,[45,46] yet a little departure from this may be anticipated due to structural constraints imposed by bi- or polydentate ligands.[46] In fact, apart from dodecahedral and square-antiprismatic structures three more geometries have been proposed[47] for eight-coordinated species. These are cubic (O_h), trigonal prismatic with ligands in the center of the two end faces (D_{3h}), and trigonal prismatic with ligands centered on two side faces (C_{2v})—all having ground states with twofold degeneracy. The paramagnetism in these compounds can be explained by assuming the molecules to have any one of the last three configurations, although this is highly speculative in the absence of crystal structure data.[48] Nevertheless, we note that recently some paramagnetic Mo(IV) complexes ($\mu_{eff} \approx 2.57$ μ_B) have been reported[19a] with distorted-pentagonal-bipyramidal geometries.

Cyclic voltammograms of Mo(IV) complexes (**5a,c,d**) in DMF/0.1 M TEAP solutions are shown in Figure 6[49] and the relevant data are summarized in Table VI. Apart from $Mo(L\text{-}Bu)_2(L\text{-}H)_2$, the electron-transfer behaviors of the other three compounds at a HMDE are almost identical, each involving two nearly reversible waves, one due to reduction ($E_{1/2} = -0.42$ V) and the other due to oxidation ($E_{1/2} = -0.2$ V). In each case the scan was initiated from −0.3 V and the natures of the voltammograms remain practically identical irrespective of the scan direction. The currents observed by differential pulse voltammetry or by cyclic voltammetry for the steps are of equal height, indicating an identical number of electrons in each step. In addition, except for $Mo(L\text{-}He)_2(L\text{-}H)$, $\Delta E_p = 70 \pm 10$ mV at low scan rates ($v < 100$ mV s^{-1}), and $i_p/v^{1/2}$ ($i_p = i_{pc} + i_{pa}$) from the cyclic voltammograms was constant for the two processes, indicating that one electron is reversibly transferred in each step.[50] Confirmation of the overall number of electrons transferred in the reduction step was obtained from controlled-potential electrolysis carried out at potentials ~200 mV more cathodic than the $E_{1/2}$ values. The results have shown that 1 mol of electrons is consumed per mole of complex. Electron stoichiometry determination for the oxidation step by potentiostatic coulometry did not yield satisfactory results, probably owing to some unidentified reaction(s). However, on the basis of coulometric, voltammetric, and differential pulse voltammetric data, the following reactions may be assigned:

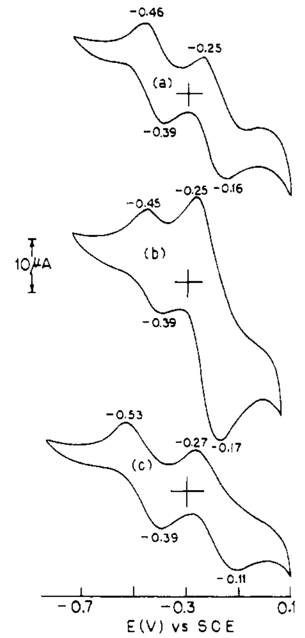

Figure 6. Cyclic voltammograms (at a HMDE, $v = 50$ mV s^{-1}) of (a) $Mo(L\text{-}Et)_2(L\text{-}H)_2$, (b) $Mo(L\text{-}Bu)_2(L\text{-}H)_2$, and (c) $Mo(L\text{-}Hx)_2(L\text{-}H)_2$ in 0.1 M TEAP/DMF.

$$Mo^{III}(L\text{-}R)_2(L\text{-}H)_2^- \xrightleftharpoons{(E_{1/2})_3} Mo^{IV}(L\text{-}R)_2(L\text{-}H)_2 + e^- \quad (3)$$

$$Mo^{IV}(L\text{-}R)_2(L\text{-}H)_2 \xrightleftharpoons{(E_{1/2})_4} Mo^{V}(L\text{-}R)_2(L\text{-}H)_2^+ + e^- \quad (4)$$

Although the reduction behavior of $Mo(L\text{-}Bu)_2(L\text{-}H)_2$ is very much identical with that of the other reported Mo(IV) complexes involving a reversible Mo(IV)–Mo(III) single-electron transfer ($E_{1/2} = -0.42$ V), its oxidation behavior is quite unique as it involves a reversible single-step two-electron transfer comprising Mo(IV)–Mo(VI) states. A linear relationship between i_p and $v^{1/2}$, identical values of i_{pa} and i_{pc}, and constant $E_{1/2}$ (within an accuracy of ±4%) for different scan rates (50–500 mV s^{-1}) were observed for this redox couple. Like other Mo(IV) complexes, coulometric confirmation of electron stoichiometry of this oxidation process is not possible due to constant coulomb count. However, the cyclic voltammetric (Figure 6) and differential pulse voltammetric current heights for this wave are twice as high as that of the reduction process, indicating that in this reaction two electrons are transferred. The related electron-transfer process is

$$Mo^{IV}(L\text{-}Bu)_2(L\text{-}H)_2 \xrightleftharpoons{2e^-} Mo^{VI}(L\text{-}Bu)_2(L\text{-}H)_2^{2+}$$

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(42) Electronic spectrum of $Mo(L\text{-}Bu)_2(L\text{-}H)_2$ is shown as a typical one. The gross features of the electronic spectra of remaining compounds (**5a**, **5b**, and **5d**) are similar.

(43) Nieuwpoort, A.; Steggerda, J. J. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 294.

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(48) $Mo(L\text{-}R)_2(L\text{-}H)_2$ compounds could not be crystallized because of their extremely low solubility in common organic solvents except DMF. All efforts to crystallize them from mixed solvent (one of which is DMF) solution lead to slow decomposition as is evident from their electronic spectra.

(49) Under identical conditions the gross voltammetric feature of $Mo(L\text{-}Pr)_2(L\text{-}H)_2$ (**5b**) is similar to that of **5a**.

(50) Matsuda, Y.; Yamada, S.; Murakami, Y. *Inorg. Chem.* **1981**, *20*, 2239 and references therein.

A possible reason for this changeover of oxidation pattern of the Mo(IV) complexes from a single- to a two-electron process is still not clear to us. Initially when we first observed this phenomenon in the butyl derivative (**5c**), we were under the impression that the size of the alkyl group had a possible role to play for this two-electron process. This has prompted us to investigate the *n*-hexyl derivative (**5d**), which only produced a one-electron-oxidation wave.

Concluding Remarks. Oxygen-transfer reactions have been successfully employed here to get a number of molybdenum compounds in the oxidation states VI, V, and IV. The sequential abstraction of oxygen atoms in going from $MoO_2(L\text{-}R)_2$ to $Mo(L\text{-}R)_2(L\text{-}H)_2$ is clearly manifested in their IR spectra (Figure 1). Mo(IV) compounds constitute the first reported example of a series of complexes with an MoS_8 chromophore having a spin triplet ground state. Electron-transfer behavior of the reported complexes show a complete changeover from an initial irreversible to a perfectly reversible type via a quasi-reversible stage as the oxygen atoms are depleted successively from the *cis*-O_2 Mo^{VI} moiety. Alkyl substitution in the ligand framework appears to have very little effect upon their magnetic, spectroscopic, and electrochemical properties except in the redox behavior of $Mo(L\text{-}Bu)_2(L\text{-}H)_2$, where a single-step two-electron reversible oxidation (Mo(IV)-(Mo(VI)) is observed. Similar redox behavior involving simultaneous two-electron transfer is well-known for many biochemical reactions catalyzed by molybdenum enzymes.[51]

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Registry No. **2a**, 97316-06-8; **2b**, 97316-07-9; **3a**, 97316-08-0; **3b**, 97316-09-1; **3c**, 97316-10-4; **3d**, 97316-11-5; **4a**, 97316-12-6; **4b**, 97316-13-7; **4c**, 97316-14-8; **4d**, 97316-15-9; **5a**, 97316-16-0; **5b**, 97316-17-1; **5c**, 97316-18-2; **5d**, 97316-19-3; $MoO_2(acac)_2$, 17524-05-9; $MoO_2(L\text{-}Et)_2$, 89742-19-8; $MoO_2(L\text{-}Bu)_2$, 89742-20-1; $Mo^VO_2(L\text{-}Pr)_2^-$, 97316-20-6; $Mo^VO_2(L\text{-}Hx)_2^-$, 97316-21-7; $Mo^VOCl_2(L\text{-}Et)_2^-$, 97316-22-8; $Mo^VOCl_2(L\text{-}Pr)_2^-$, 97316-23-9; $Mo^VOCl_2(L\text{-}Bu)_2^-$, 97316-24-0; $Mo^VOCl_2(L\text{-}Hx)_2^-$, 97316-25-1; $Mo^{III}(L\text{-}Et)_2(L\text{-}H)_2^-$, 97316-26-2; $Mo^{III}(L\text{-}Pr)_2(L\text{-}H)_2^-$, 97316-27-3; $Mo^{III}(L\text{-}Hx)_2(L\text{-}H)_2^-$, 97316-28-4; $Mo^V(L\text{-}Et)_2(L\text{-}H)_2^+$, 97316-29-5; $Mo^V(L\text{-}Pr)_2(L\text{-}H)_2^+$, 97316-30-8; $Mo^V(L\text{-}Hx)_2(L\text{-}H)_2^+$, 97316-31-9; $Mo^{VI}(L\text{-}Bu)_2(L\text{-}H)_2^{2+}$, 97316-32-0.

Supplementary Material Available: A listing of analytical data for the compounds (Table I) (1 page). Ordering information is given on any current masthead page.

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Formation and NMR Spectra of Platinum(II)-Tripeptide Complexes

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Triglycine (G_3^-) reacts with $PtCl_4^{2-}$ to give complexes with two deprotonated-N(peptide) bonds to Pt(II). Three species, with relative concentrations $Pt^{II}(H_{-2}G_3)Cl^{2-} > Pt^{II}(H_{-2}G_3)^- > Pt^{II}(H_{-2}G_3)(OH)^{2-}$, are identified from ^{13}C, ^1H, and ^{195}Pt NMR and the measurement of released Cl^- and H^+. These complexes cause an enormous upfield shift of −7144 to −7517 ppm in ^{195}Pt NMR peaks (relative to $PtCl_6^{2-}$). This shift is much larger than that caused by cyanide ion in $Pt(CN)_4^{2-}$ and indicates the high donor strength of the deprotonated-N(peptide) group. The pK_a of the peptide group, when it bonds to Pt(II), is between 1 and 2 in the presence of $\sim 4 \times 10^{-4}$ M Cl^-. The acid dissociation rate constant of the $Pt^{II}(H_{-2}G_3)Cl^{2-}$ complex increases from 6×10^{-5} s^{-1} in 0.10 M acid to 3×10^{-3} s^{-1} in 2.5 M acid. The CD spectra of complexes with GAG^- and GGA^- (A = L-alanyl) also indicate the coordination of two deprotonated peptide nitrogens to platinum.

Introduction

There has been a great deal of interest in the bioinorganic complexes of platinum(II)[1] since the first report[2] of the antitumor activity of *cis*-diamminedichloroplatinum(II). Much of the work has concerned platinum(II) complexes of nucleotides,[3-5] amino acids,[6] and peptide esters.[7]

Several dipeptide complexes have been found that contain deprotonated peptide nitrogens bound to platinum. The crystal structure[8,9] of $Pt^{II}(H_{-1}GM)Cl^-$ shows that the amine nitrogen, peptide nitrogen, and thioether sulfur are coordinated. On the basis of IR and elemental analysis data, a similar complex forms with L-alanyl-L-methionine (AM^-).[10] Diglycine (G_2^-) forms a bis complex, *trans*-[$Pt(G_2)_2Cl_2^{2-}$], which on the addition of hot KOH solution yields *trans*-[$Pt^{II}(H_{-1}G_2)_2^{2-}$].[11] Dipeptides have also been shown to bridge two Zeise's salt ($K[PtCl_3(C_2H_4)]$) residues. Coordination is through the amine nitrogen and peptide oxygen to one platinum(II) and through the peptide nitrogen and carboxylate oxygen to the second platinum(II).[12]

Is is surprising, given the work with dipeptide complexes, that no tripeptide (L^-) complexes of the form, $Pt^{II}(H_{-2}L)^-$, have been reported. Deprotonation of the peptide nitrogen to form Pt^{II}-

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