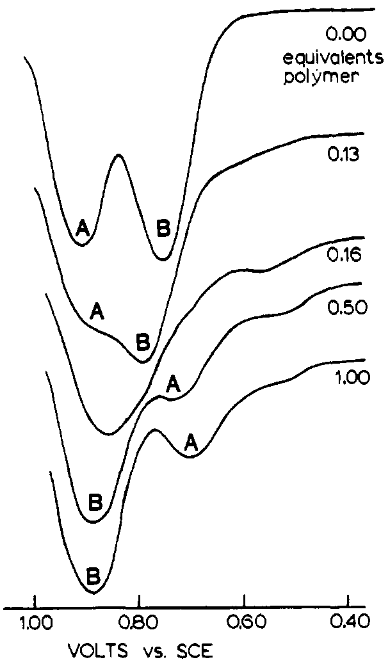


Figure 2. Representative differential-pulse voltammograms for 2 mM *trans*-(py)$(NH_3)_4$Ru(NCpy)Ru$(bpy)_2Cl^{5+/4+/3+}$ in nitromethane (0.1 M TEAH) with added poly(ethylene glycol) (equivalents are indicated on the figure). Peak A is the *trans*-(py)$(NH_3)_4Ru^{II/III}$– couple. Peak B is the $(bpy)_2ClRu^{II/III}$– couple.

(characteristic of the $(bpy)_2ClRu^{2+/+}$– fragment) was observed for the second reduction peak in pure NM and for the first peak in NM + crown.

Studies with poly(ethylene glycol) yielded a somewhat different behavior. DPV peaks were still observed to (a) shift negatively for $Ru(NH_3)_5py^{3+/2+}$ and (b) remain unchanged for $(bpy)_2ClRu(NCpy)^{2+/+}$. However, for the mononuclear ammine complex, a progressive (rather than stepwise) shift in E_f with increasing polymer concentration was found. Furthermore, somewhat less than 1 equiv of polymer was required in order to reach a limiting electrochemical response. As suggested by Figure 2, these same effects are manifest in the binuclear complex as a progressive shift (and eventual crossing) of differential pulse voltammetry peaks with increasing concentration of poly(ethylene glycol)—limiting behavior again appearing at concentrations well below 1 equiv. The "crossing" effect, together with the $Ru(NH_3)_5py^{3+/2+}$ and $(bpy)_2ClRu(pyCN)^{2+/+}$ results, provides clear evidence for binding-induced redox isomerization in the binuclear complex (cf. eq 2). The gradual nature of the shifts in E_f strongly suggests, however, that bound and free ammine-containing complexes (mononuclear as well as binuclear) are able to exchange rapidly between the polymer and solution environments. The observation that less than 1 equiv of poly(ethylene glycol) is needed to achieve apparently complete binding is broadly consistent with the idea that each polymer strand may bind multiple complexes. Note that each strand comprises, on average, roughly 200 repeating units.

Finally, the overall energetic basis for redox isomerization in the various solvation and ligation environments merits discussion. The redox energetics for $(py)(NH_3)_4Ru(NCpy)Ru(bpy)_2Cl^{4+}$ can perhaps best be understood by comparison to $(NH_3)_5$Ru(pyrazine)Os$(bpy)_2Cl^{4+}$.[1] Replacement of osmium by ruthenium causes a 0.4 V increase in redox potential at the polypyridyl end. This is approximately offset at the ammine end by replacement of NH_3 by pyridine ($\Delta E \approx 0.15$ V)[9] and pyrazine by the nitrile-bound cyanopyridine ($\Delta E \approx 0.13$ V).[29]

Acknowledgment. We thank Dr. Dong Yoon for supplying a sample of dibenzo-36-crown-12. J.C.C. acknowledges support from a PPG Industries Foundation Grant of the Research Corp. J.T.H. acknowledges support from the Department of Energy, Office of Energy Research, Division of Chemical Sciences (Grant No. DEFG02-87ER 13808). The modified CARY 14 spectrophotometer was obtained with funds from an NSF equipment grant (Grant No. CHE-87722985) and from a Presidential Young Investigator Award. The Raman facilities are part of the Materials Research Center at Northwestern (Grant NSF-DMR-8821571).

---

(29) The estimate here is fairly crude: studies of linkage isomers[12] suggest that replacement of a symmetrical bridge by the asymmetric 4-cyanopyridine ligand will lead, in a net sense, to a ΔE contribution of ~0.13 V.

Contribution from the Department of Chemistry,
The University of Queensland, Brisbane, Australia 4072

Photoisomerization and Other Reactions of Dimethylplatinum(IV) Complexes with Iminodiacetate and (Methylimino)diacetate

Trevor G. Appleton,* Ron D. Berry, John R. Hall, and Jacqueline A. Sinkinson

Received February 7, 1991

The ligands L^{2-}, $RN(CH_2CO_2^-)_2$ (R = CH_3, H), react with a solution of $[\{Pt(CH_3)_2(OH)_2\}\cdot 1.5H_2O]_n$ in alkali to give initially $Pt(CH_3)_2(OH)_2$(L-*N*,*O*)$^{2-}$ in which the ligand coordinates bidentate trans to the methyl groups. Ring closure to form $Pt(CH_3)_2(OH)$(L-*N*,*O*,*O'*)$^-$ is very slow under alkaline conditions, but is much faster in acid solution, to give $Pt(CH_3)_2(H_2O)$(L-*N*,*O*,*O'*) (N trans to methyl). *fac*-$Pt(CH_3)_2Br(H_2O)_3^+$ with LH^- gives $Pt(CH_3)_2Br$(L-*N*,*O*,*O'*)$^-$ (*N* trans to methyl). Irradiation with a mercury lamp causes facile isomerization to the isomer with N trans to bromide. This reaction occurs without dissociation of L^{2-}. A side reaction at high pH produces $Pt(CH_3)_2(OH)$(L-*N*,*O*,*O'*)$^-$ (N trans to hydroxide). The colorless aqua complexes $Pt(CH_3)_2(H_2O)(L)$ are photoisomerized much less efficiently than the pale yellow bromo complexes. Thermal isomerizations are very much slower.

Introduction

There has recently been considerable interest in the complexes of platinum with the versatile ligand iminodiacetate and its *N*-alkyl derivatives.[1-4] In square-planar platinum(II) complexes, these ligands are either bidentate, coordinating through nitrogen and one carboxylate oxygen,[1-4] or meridionally tridentate.[1] In octahedral complexes (e.g., with cobalt(III)),[5] facial tridentate coordination is typical. This coordination mode has been observed

---

(1) Appleton, T. G.; Berry, R. D.; Hall, J. R. *Inorg. Chem.* **1985**, *24*, 666.
(2) Hoeschele, J. D.; Farrell, N.; Turner, W. R.; Rithner, C. D. *Inorg. Chem.* **1988**, *27*, 4106.
(3) Khokhar, A. R.; Lumetta, C. J.; Newman, R. A.; Doran, S. L. *Inorg. Chim. Acta* **1988**, *151*, 249.
(4) Appleton, T. G.; Hall, J. R.; Ralph, S. F. *Inorg. Chem.* **1985**, *24*, 673.
(5) Legg, J. I.; Cooke, D. W. *Inorg. Chem.* **1966**, *5*, 594.

0020-1669/91/1330-3860$02.50/0

for the octahedral platinum(IV) complexes *fac*-$PtY_3(L)^-$ (**3**, **4**), where Y = Cl,[1] CH_3,[6] and LH_2 = $RN(CH_2CO_2H)_2$ (R = H, iminodiacetic acid, $idaH_2$; R = CH_3, (methylimino)diacetic acid, $midaH_2$). In each of these platinum(IV) complexes, all three coordination sites offered to the tridentate ligand are identical, although the properties of the ligands Y trans to the donor atoms of L^{2-} are very different. The methyl ligand has a very high trans effect,[7] so that metal–ligand bonds trans to methyl are much more labile than those trans to halide.

cis-dimethylplatinum(IV) complexes are unusual in that, in the one compound, there are coordination sites which are labile (trans to the methyl groups) and coordination sites which are relatively inert (cis to methyl). The chemistry of dimethylplatinum(IV) complexes is therefore dominated by the different rates of reaction at these coordination sites. Reactions trans to methyl usually occur rapidly at room temperature, while reactions cis to methyl, if they occur at all, usually require long standing and/or heating.[8-10] Reactions may be easily followed by NMR since, in addition to signals from ligand nuclei, ^1H and $^{13}C\{^1H\}$ spectra show for each chemically distinct methyl group a singlet flanked by "satellites" from coupling with ^{195}Pt ($I = {}^1/_2$, 34% abundance). The values of $^2J(Pt–CH_3)$ provide a reliable indication of the ligand trans to the methyl group.[11] The one-bond Pt–C coupling constant is less useful, as it is affected to a much greater extent by ligands cis to methyl.[9,12]

We have previously studied[13,14] the reactions of glycinate with the convenient dimethylplatinum(IV) starting complexes *fac*-$Pt(CH_3)_2Br(H_2O)_3{}^+$ (**1**) and "*cis*-$Pt(CH_3)_2(OH)_4{}^{2-}$" (**2**).[15] Even with this relatively simple bidentate ligand, the interactions with labile and inert coordination sites produce a rich chemistry.

In the present work, we set out to investigate the reactions of the iminodiacetate ligands with **1** and **2**. In the course of this work, we found that some of the reaction products undergo facile photoisomerization reactions. We have previously described[16] the use of related photolabilization reactions in preparing dimethylplatinum(IV) cyanide complexes.

Experimental Section

Starting Materials. $[Pt(CH_3)_2Br_2]_n$ and $[\{Pt(CH_3)_2(OH)_2\}\cdot 1.5H_2O]_n$ were prepared as previously described.[17] A solution of *fac*-$[Pt(CH_3)_2Br(H_2O)_3](NO_3)$ was prepared by reaction of an aqueous acetone suspension of $[Pt(CH_3)_2Br_2]_n$ with 1 mol equiv of silver nitrate.[8] The filtrate after removal of silver bromide was concentrated under reduced pressure and then made up to a standard volume with H_2O in a volumetric flask. On the assumption that reaction with the silver ion was quantitative, this allowed the concentration of the solution to be estimated. A similar procedure using D_2O instead of H_2O was used to prepare a solution of *fac*-$[Pt(CH_3)_2Br(D_2O)_3](NO_3)$ in D_2O. The ligands were used as supplied ($idaH_2$, Fluka; $midaH_2$, Aldrich).

NMR Spectra. The 400-MHz ^1H and 100.4-MHz ^{13}C NMR spectra were obtained with the use of a JEOL GX-400 spectrometer, with a dual $^1H/^{13}C$ 5-mm probe or (for some ^{13}C spectra) a broad-band tunable 10-mm probe. The spectrometer was locked on deuterium from solvent D_2O. For the ^1H spectra, 16 scans were used, with tilt of the magnetization vector of 45°, 32K data points, and spectrum width of 5000 Hz. For the ^{13}C spectra, overnight runs were used (approximately 12000 pulses 3-s apart, with a 40° tilt of the magnetization vector, 64K data points, and spectrum width of 24000 Hz). Some ^{13}C spectra were run at 25.05 MHz on a JEOL FX-100 instrument, under conditions previously described.[1] Unless otherwise stated, all ^{13}C spectra were proton-decoupled. ^{13}C shifts are reported relative to external tetramethylsilane, with internal dioxane taken as 67.73 ppm. The 100-MHz ^1H spectra were run on a JEOL PS-100 continuous-wave instrument locked on the ^1H peak of solvent HDO or on the JEOL FX-100 instrument locked on solvent deuterium. ^1H shifts are reported relative to internal sodium 3-(trimethylsilyl)propanesulfonate (TSS). All shifts are positive to lower shielding.

Irradiation Experiments. A 1-L Hanovia photochemical reactor was used, which was fitted with a medium-pressure mercury discharge lamp rated at 125 W, with a water-filled cooling jacket with outer walls of silica. Samples were irradiated in 5-mm glass NMR tubes held at a distance of 2.5 cm from the outer jacket. Most of the UV radiation would be expected to be absorbed by the Pyrex glass, so that the dominant wavelengths of transmitted light would be 365 and 436 nm for a sample in an NMR tube. In some experiments, there was significant deposition of solid material on the tube walls, which reduced the efficiency of the irradiation. The solutions were then periodically filtered into fresh NMR tubes.

Other Techniques. IR spectra were recorded with the use of a Perkin-Elmer 1600 Fourier transform spectrometer, either on pressed KBr disks or on Nujol mulls held between KBr plates. Microanalyses were carried out by the microanalytical service in this department and by the Australian Microanalytical Service, Melbourne, Australia. Routine pH measurements were made with narrow-range indicator strips supplied by Riedel-de-Haen and Merck, and more accurate measurements were made with an Ionode combination glass/reference electrode and a TPS 1820 mV pH meter. UV–visible spectra were recorded on a Shimadzu UV-265 spectrometer between 500 and 200 nm, using 1-cm quartz cells. HPLC purifications were carried out with a Whatman Partisil-10 semipreparative column, with H_2O/CH_3OH solvent and an isocratic flow of 1 mL/min, with eluant monitored at 210 nm.

Preparation of $Pt(CH_3)_2(H_2O)(L)$ (N Trans to Methyl) (8a,b). $[\{Pt(CH_3)_2(OH)_2\}\cdot 1.5H_2O]_n$ (0.184 g, 0.64 mmol) was suspended in 2 mL of water. One mole equivalent of KOH was added in aqueous solution, which caused the solid to dissolve. Solid $midaH_2$ (0.094 g, 0.64 mmol) was dissolved in an aqueous solution containing 1 mol equiv of KOH, and the two solutions were mixed. The solution was stirred as 5 M HNO_3 solution was added, until the pH reached 3.5. Some solid sometimes precipitated during the acid addition but redissolved to give a clear colorless solution, which was allowed to stand. Over 2 days, a colorless crystalline solid formed. The supernatant liquid was removed with a Pasteur pipette, and the solid was washed with small portions of cold water and then acetone and dried in a vacuum desiccator over silica gel. Yield was 0.111 g (45%). The product, $Pt(CH_3)_2(H_2O)(mida)$ (**8a**) was sparingly soluble in water, but dissolved easily in dilute alkali. It was insoluble in acetone. Its IR spectrum showed a broad band at 1628 cm^{-1} from C=O stretching and a broad O—H stretching band at 3434 cm^{-1}.

The preparation of $Pt(CH_3)_2(H_2O)(ida)$ (**8b**) differed from that for the mida analogue described above only in that the final product was more soluble and did not crystallize from solution. After a solution had been allowed to stand for 2 days at pH 3.5, it was concentrated in a stream of air to approximately 2 mL, whereupon acetone was added to precipitate the product, which was filtered off, washed with acetone, and dried as before. Yield was 91%. Its IR spectrum showed a strong broad ν(O–H) band from coordinated water at 3434 cm^{-1} and strong bands from ν(C=O) at 1645 and 1615 cm^{-1}.

Preparation of $K[Pt(CH_3)_2Br(L)]$ (N Trans to Methyl) (9a,b). To a solution of $[Pt(CH_3)_2Br(H_2O)_3](NO_3)$ (0.45 mmol in 10 mL water) was added 0.056 g of $midaH_2$ (0.38 mmol) in 25 mL of water. The solution was heated in the dark at 70–80 °C for 20 min, and then 1 M KOH solution was added slowly with stirring until the pH reached 5. The solution was filtered from small amounts of pale yellow solid ($[Pt(CH_3)_2Br(OH)]_n$), which sometimes precipitated, and then evaporated to dryness in a stream of air. The solid residue was dried in a vacuum desiccator over silica gel, then extracted with dry methanol (5 × 10 mL). The combined methanol extracts were filtered, and the solution was evaporated to dryness in a stream of air to give a pale yellow solid (0.17 g). Analytical results and the presence of bands in the IR spectrum in the region 1350–1450 cm^{-1} showed that the sample was contaminated with small amounts of KNO_3. Such samples could be used for some purposes (e.g., qualitative irradiation experiments where the course of the reaction was followed by NMR). Analytically pure samples of $K[Pt(CH_3)_2Br(mida)]$ (**9a**) were obtained by elution of a solution through a HPLC column, followed by evaporation to dryness of the appropriate

---

(6) Appleton, T. G.; Hall, J. R.; Lambert, L. *Inorg. Chim. Acta* **1978**, *29*, 89.

(7) Glass, G. E.; Schwabacher, W. B.; Tobias, R. S. *Inorg. Chem.* **1968**, *7*, 2471.

(8) Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1977**, *139*, 403.

(9) Agnew, N. H.; Appleton, T. G.; Hall, J. R. *Aust. J. Chem.* **1982**, *35*, 881.

(10) Appleton, T. G.; Hall, J. R.; Ham, N. S.; Hess, F. W.; Williams, M. A. *Aust. J. Chem.* **1983**, *36*, 673.

(11) Clegg, D. E.; Hall, J. R.; Swile, G. A. *J. Organomet. Chem.* **1972**, *38*, 403.

(12) Clark, H. C.; Manzer, L. E.; Ward, J. E. H. *Can. J. Chem.* **1974**, *52*, 1973.

(13) Agnew, N. H.; Appleton, T. G.; Hall, J. R. *Inorg. Chim. Acta* **1980**, *41*, 71.

(14) Agnew, N. H.; Appleton, T. G.; Hall, J. R. *Inorg. Chim. Acta* **1980**, *41*, 85.

(15) "$Pt(CH_3)_2(OH)_4{}^{2-}$" will be used for convenience to represent the complex mixture of hydroxo complexes obtained when $[\{Pt(CH_3)_2(OH)_2\}\cdot 1.5H_2O]_n$ is dissolved in dilute alkali. See ref 9.

(16) Appleton, T. G.; Hall, J. R.; Williams, M. A. *Aust. J. Chem.* **1987**, *40*, 1565.

(17) Hall, J. R.; Hirons, D. A.; Swile, G. A. *Inorg. Synth.* **1980**, *20*, 185.

Table I. Selected NMR Data[a]

			Pt–CH_3			N–CH_3[b]		carboxyl	
compound	structure	pD	δ(H)	^2J(Pt–CH_3), Hz	donor atom trans to CH_3	δ(H)	*J*(Pt–N–CH_3),[c] Hz	δ(*C*)	*J*(Pt–C),[c] Hz
$PtCl_3$(mida-*N,O,O'*)$^{-d}$	**3a**	7	...	...		3.19	27.5	182.43	8.8
$Pt(CH_3)_3$(mida-*N,O,O'*)$^{-e}$	**4a**	7	0.79	76.6	O	2.70	17.3	183.37	<4
			0.93	69.1	N				
$Pt(CH_3)_2(OH)_2$(mida-*N,O*)$^{2-f}$	**5a**	10	1.36	76.3	O	2.68	8.2	184.15	<8
			1.48	70.8	N			177.29	~11
$Pt(CH_3)_2(OH)$(mida-*N,O,O'*)$^{-f}$	**6a**	10	1.50	77.5	O	2.86		185.72	
			1.58	70.2	N			182.60	
$Pt(CH_3)_2(H_2O)_2$(midaH-*N,O*)$^+$	**7a**	3.5	1.92	77.5	O	3.07		*g*	
			1.77	72.0	N				
$Pt(CH_3)_2(H_2O)$(mida-*N,O,O'*)	**8a**	2.5	1.70	75.1	O	2.96	10.6	*g*	
			1.80	67.1	N				
$Pt(CH_3)_2Br$(mida-*N,O,O'*)$^-$	**9a**	5	1.65	76.3	O	2.95	13.1	185.63	11.7
			1.75	67.8	N			182.59	<5
$Pt(CH_3)_2Br$(mida-*N,O,O'*)$^-$	**11a**	7	1.61	76.0	O	2.76	47.0	181.62	13.7
$Pt(CH_3)_2(OH)$(mida-*N,O,O'*)$^-$	**12a**	12	1.43	78.0	O	2.72		*g*	
$Pt(CH_3)_2(H_2O)$(mida-*N,O,O'*)	**13a**	3	1.64	~72	O	2.76	54	*g*	

[a] Spectra run in D_2O, unless otherwise noted. [b] For mida complexes. [c] Where "satellite" peaks observed. [d] From ref 1. [e] From ref 6. [f] ^{13}C spectrum run in ^1H_2O. [g] ^{13}C spectrum not obtained.

fractions in a stream of air. The IR spectrum showed peaks at 1647 and 1608 cm^{-1}.

A similar procedure was used to prepare K[$Pt(CH_3)_2Br$(ida)] **9a**. Its IR spectrum showed a N–H stretching band at 3242 cm^{-1} and a strong broad band at 1637 cm^{-1}.

Preparation of K[$Pt(CH_3)_2Br$(mida)] (N Trans to Br) (11a). A solution of K[$Pt(CH_3)_2Br$(mida)] (**9a**) (0.1882 g) in 0.5 mL of D_2O in a 5-mm-diameter glass NMR tube was irradiated as described above, until the isomerization to **11a** was complete (as monitored by ^1H NMR). The solution was filtered to remove a small amount of dark, insoluble material and then evaporated to dryness in a stream of air. The residue was washed with dry methanol (which would remove any remaining isomer **9a** present). Water (5 mL) was then added to the residue. A small amount of insoluble material was filtered off, the filtrate was evaporated to dryness, and the resulting solid was dried in a vacuum desiccator over silica gel. The product, K[$Pt(CH_3)_2Br$(mida)] (**11a**) was an off-white solid. Yield was 0.0888 g (47%). Its IR spectrum showed ν(C=O) bands at 1630 and 1654 cm^{-1}.

Thermal Isomerization Reactions. Solutions in D_2O were heated in 5-mm-diameter NMR tubes clampled at a constant depth in a water bath maintained at 90–95 °C. In some prolonged experiments where decomposition occurred and solids slowly deposited, the solutions were periodically filtered through cotton wool plugs.

Mixed-Ligand Irradiation Experiments. A solution of K[$Pt(CH_3)_2Br$(mida)] (**9a**) (0.064 g, 0.131 mmol) and 0.035 g of idaH_2 (0.263 mmol) in 0.5 mL of D_2O was prepared, and the pD was adjusted to 10 by addition of a solution of KOH in D_2O. The solution was filtered through a cotton wool plug into a 5-mm-diameter glass NMR tube and irradiated as described above for 7 min, after which the solution was examined by ^1H NMR spectroscopy. An analogous experiment was carried out in which K[$Pt(CH_3)_2Br$(ida)] (**9b**) was irradiated in the presence of mida^{2-}.

Results

Selected NMR data are presented in Table I. In 100-MHz ^1H NMR spectra, the "satellite" peaks from coupling with ^{195}Pt were always sharp. In 400-MHz spectra, the satellite peaks from dimethylbromoplatinum(IV) complexes were only slightly broadened, but in spectra of complexes with aqua or hydroxo ligands cis to the methyl groups, the satellite peaks were significantly broadened. This broadening can be attributed to chemical shift anisotropy induced relaxation of the ^{195}Pt nuclei.[18] The relaxation rate increases with the square of the magnetic field strength. Since the contribution of bromide to ^{195}Pt chemical shifts is intermediate between the effects of methyl and aqua/hydroxo,[9] there will be a smaller difference between the contributions to the metal chemical shift along the *z* and *x,y* axes in the dimethylbromoplatinum complexes compared with dimethylhydroxo- or dimethylaquaplatinum complexes. As well, the aqua or hydroxo ligands may be involved in hydrogen bonding with solvent water, which may slow down the rate of tumbling of the ion in solution.

For Pt–CH_3 and N–CH_3 peaks in ^1H spectra and for carbon peaks, it was usually possible to measure coupling constants to ^{195}Pt from low-field spectra. For the more complex ^1H spectra from methylene groups, it was frequently necessary to obtain high-field spectra to provide sufficient dispersion to allow analysis of the spectrum, but this often meant that peaks from coupling to ^{195}Pt were not observed. When the nitrogen atom of the ligand binds to a metal, there is no longer rapid inversion about nitrogen. The adjacent methylene protons are then diastereotopic. Khokhar et al.[3] erroneously ascribe the observed nonequivalence of methylene protons in the uncoordinated arm of [(amine)$_2$Pt(OC(O)-$CH_2N(R)CH_2CO_2$)] to restricted rotation about the C–N bond, but these protons cannot be made equivalent by such rotation. For all of our complexes, we observed the expected AB pattern for each distinct methylene group, except for some of the mida complexes for which one methylene group sometimes gave a "deceptively simple" singlet ($(\nu_A - \nu_B) \ll |J_{AB}|$). Details are given in supplementary data. When D_2O solutions of the complexes were allowed to stand for long periods at high pD or solutions in D_2O were heated, the methylene protons were replaced by deuterium. Under comparable conditions, this reaction occurred more readily with mida complexes than their ida analogues.

Dimethylhydroxo- and Dimethylaquaplatinum(IV) Complexes (Scheme I). When 1 mol equiv of midaH_2 in a solution of KOH in D_2O was added to a solution of **2** ([{$Pt(CH_3)_2(OH)_2$}·1.5H_2O]$_n$) dissolved in KOH/D_2O (final pD approx. 10), an immediate reaction occurred to give a complex formulated as $Pt(CH_3)_2(OH)_2$(mida)$^{2-}$ (**5a**). The ^1H NMR spectrum showed two singlets with satellites from the Pt–CH_3 groups, with Pt–CH_3 coupling constants corresponding to methyl groups trans to N (70.8 Hz) and trans to carboxylate O (76.3 Hz). The methylene protons showed one AB pattern and a "deceptively simple" singlet. The low value of the Pt–N–CH_3 coupling constant, 8.2 Hz (cf. 17.3 Hz in $Pt(CH_3)_3$(mida)$^-$ (**4a**),[6] 27.5 Hz in $PtCl_3$(mida)$^-$ (**3a**)[1]) is consistent with coordination of nitrogen trans to the high trans influence ligand, methyl.

Since it was difficult to keep a D_2O solution for long periods without methylene group deuteration, a solution in H_2O was used to obtain a ^{13}C spectrum. This showed, in addition to the expected signals from Pt–CH_3 and N–CH_3, two methylene signals and two carboxyl peaks. One of the carboxyl peaks occurred at 184.15 ppm. A peak at such low shielding corresponds to a carboxyl carbon in a five-membered chelate ring.[19,20] The other carboxyl peak was at 177.29 ppm, corresponding to a carboxyl carbon atom

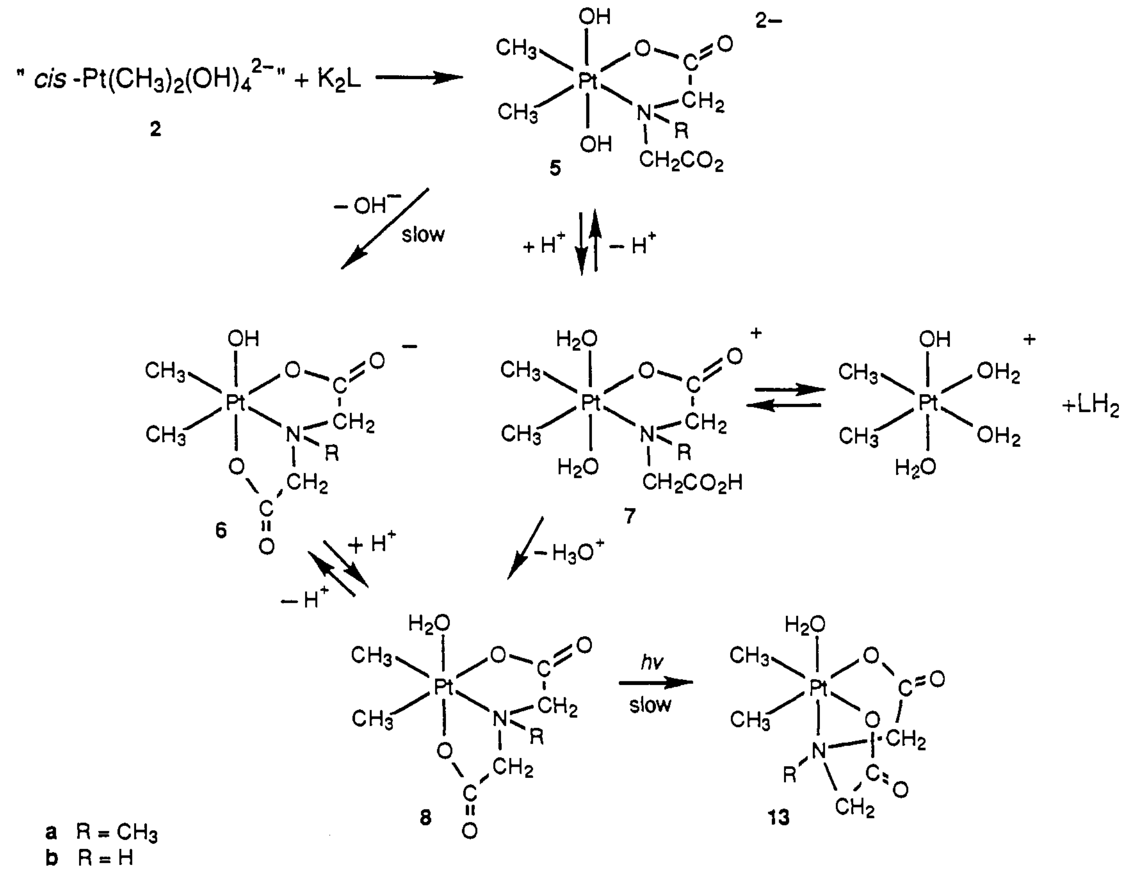
---

(18) Lallemand, J.-Y.; Soulie, J.; Chottard, J.-C. *J. Chem. Soc., Chem. Commun.* **1980**, 436.

(19) Howarth, O. W.; Moore, P.; Winterton, M. *J. Chem. Soc., Dalton Trans.* **1974**, 2271.

(20) Appleton, T. G.; Hall, J. R.; Prenzler, P. D. *Inorg. Chem.* **1989**, *28*, 815.

Scheme I



not incorporated in a five-membered ring.

The only structure consistent with all these NMR data is **5a**, in which mida^{2-} has formed a N,O-chelate ring trans to the methyl groups.

When the solution was allowed to stand for several days at pH 10, new peaks grew slowly in the NMR spectra, which were assigned to complex **6a**, in which mida^{2-} is tridentate. The Pt–CH$_3$ coupling constants (Table I) still corresponded to methyl groups trans to N and carboxylate O, and the methylene protons showed an AB spectrum and a "deceptively simple" singlet. The ^{13}C spectrum showed two carboxyl carbon signals, at 185.7 and 182.6 ppm, corresponding to the two different five-membered chelate rings in **6a**.

Acidification of a freshly prepared D_2O solution of **5a** with dilute D_2SO_4 caused partial dissociation of the (methylimino)diacetate ligand, and $[\{Pt(CH_3)_2(OD)_2\}\cdot mD_2O]_n$ began to precipitate at pD 8, redissolving at pD 6. At pD 3.5, the ^{1}H NMR spectrum showed a singlet with satellites from the methyl groups of $Pt(CH_3)_2(OD)(D_2O)_3^+$ (δ 1.83; $^2J(Pt–CH_3) = 78$ Hz[9]), peaks from free midaD$_2$, and a set of peaks assignable to $Pt(CH_3)_2(D_2O)_2$(midaD-*N*,*O*)$^+$ (**7a**), the protonated form of **5a**. Within a few minutes, a new set of peaks began to grow, from $Pt(CH_3)_2(D_2O)$(mida-*N*,*O*,*O'*) (**8a**), and this nonelectrolyte complex began to precipitate from solution. A sample similarly prepared from ^1H_2O solution gave microanalytical results corresponding to this formulation. The same solid was obtained if $[\{Pt(CH_3)_2(OH)_2\}\cdot 1.5H_2O]_n$ was dissolved in an aqueous solution of midaH$_2$. The ring closure reaction to form **8a** was very much faster than the corresponding reaction under alkaline conditions to form **6a**. In glycinate complexes, such as $Pt(CH_3)_2(OH)_2$(gly-*N*)$_2^{2-}$, ring closure involving displacement of "inert" Pt–OH by carboxylate does not occur.[11,21]

Solid **8a** was only sparingly soluble in water, but dissolved readily in alkaline solution to give $Pt(CH_3)_2(OH)$(mida-*N*,*O*,*O'*)$^-$ (**6a**). The IR spectrum of **8a** did not show any ν(C=O) peak above 1700 cm^{-1}, in the region expected for free –COOH,[22] and did show peaks near 3400 cm^{-1} from coordinated water.

Analogous reactions occurred with iminodiacetic acid. The nonelectrolyte complex $Pt(CH_3)_2(H_2O)$(ida-*N*,*O*,*O'*) (**8b**) was much more soluble than the mida analogue and precipitated only from very concentrated solution.

Reactions of *fac*-$Pt(CH_3)_2Br(H_2O)_3^+$ (1) with LH$_2$ (Scheme II). Reaction of equimolar quantities of **1** and midaH$_2$ in D_2O, with periodic additions of a solution of KOH in D_2O to maintain pD near 5, gave, after 3 days, a solution of $Pt(CH_3)_2Br$(mida-*N*,*O*,*O'*)$^-$ (**9a**). All NMR data (Table I) were consistent with this formulation. The tridentate coordination of the ligand was confirmed by the presence of two carboxylate peaks at low shielding. The absence of a Pt–OH$_2$ group that could deprotonate was confirmed by the absence of any change in the spectra when the pD of a solution was increased to 12. A pure sample of K[$Pt(CH_3)_2Br$(mida)] (**9a**) could be isolated from the solution with the use of HPLC and gave a satisfactory microanalysis. The IR spectrum showed no peaks attributable to water, and no ν(C=O) peak above 1700 cm^{-1} assignable to –COOH.[22]

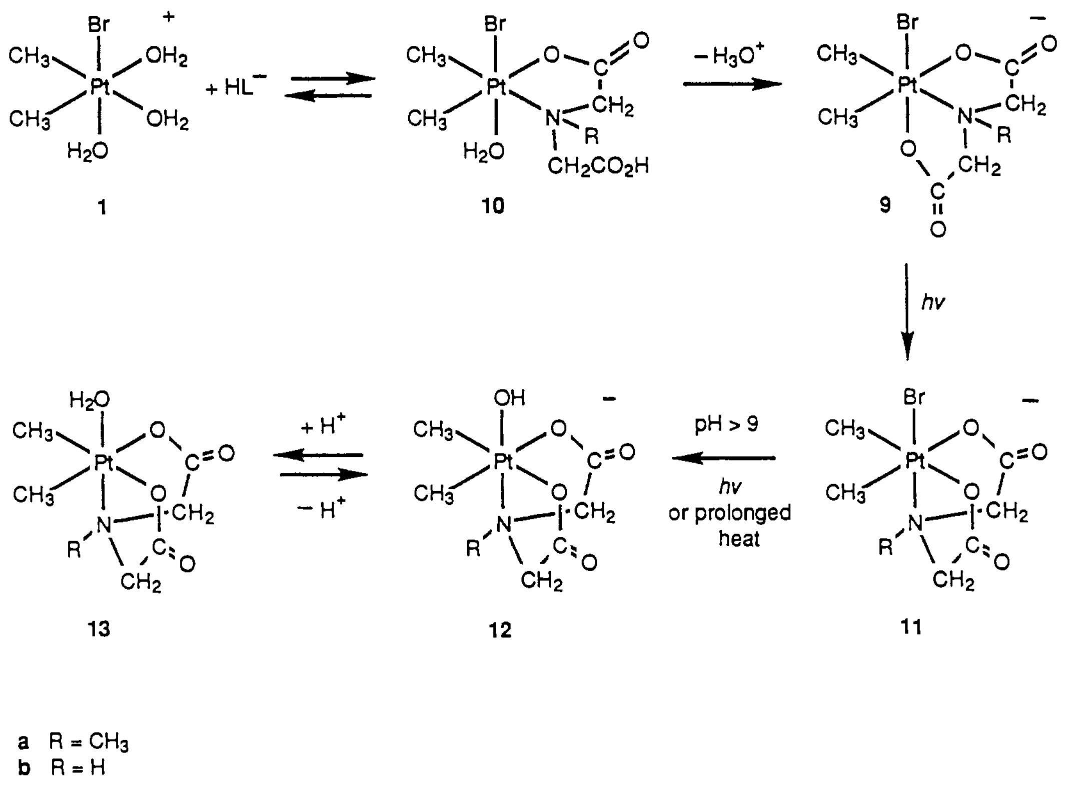
Reaction of midaH$^-$ with **1** to give **9a** was much faster if the mixture was heated before base was added. Analogous reactions occurred with ida. In solutions of idaH$_2$ with **1**, weak Pt–CH$_3$ peaks were observed (1.59, 1.47 ppm) in ^{1}H NMR spectra soon after addition, which disappeared once the peaks from $Pt(CH_3)_2Br$(ida-*N*,*OO'*)$^-$ (**9b**) (1.52, 1.49 ppm) became dominant. These weak peaks were assigned to the intermediate complex $Pt(CH_3)_2Br(D_2O)$(idaD-*N*,*O*) (**10b**) with the ligand bidentate. Two geometrical isomers are possible, depending on the orientations of the substituents on nitrogen with respect to Br. Peaks from only one were observed, probably that illustrated in Scheme II, in which the bulky bromide ion is well removed from the –CH$_2$CO$_2$H group. As well, there could be some intramolecular hydrogen bonding between the carboxyl group and the coordinated

---

(21) Grinberg, A. A.; K'ang, Y. *Zh. Neorg. Khim.* **1962**, *7*, 2304.

(22) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986; p 237.

Scheme II



water molecule. An analogous complex, **10a**, was not observed in the corresponding reaction with mida, but was presumably present in small proportions as an intermediate. Relative to the ida complex, the mida compound may be destabilized by steric interactions between the *N*-methyl group and bromide.

Photoisomerization of $Pt(CH_3)_2X(L)^-$. When a D_2O solution of $K[Pt(CH_3)_2Br(mida)]$ (**9a**) was irradiated with a mercury lamp for several minutes at pD 9, a new set of peaks appeared in the NMR spectra that corresponded to the isomer of $Pt(CH_3)_2Br(mida)^-$ with the N atom coordinated trans to bromide, **11a**. The ^1H spectrum showed only one singlet with satellites from the Pt–CH_3 groups, with $^2J(Pt-CH_3)$ = 76.0 Hz, corresponding to methyl trans to carboxylate. The ^1H spectrum showed only one AB pattern for the methylene protons (with additional peaks from platinum coupling). The Pt–N–CH_3 coupling constant, 47.0 Hz, was very much larger than in those complexes where nitrogen is bound trans to methyl. Only one methylene peak and one carboxyl peak (each with satellites) were observed in the ^{13}C spectrum, and the low shielding of the carboxylate carbon (181.6 ppm) indicated that it was part of a chelate ring. The complex could be isolated from solution as the potassium salt, which gave satisfactory analytical results.

A byproduct of the irradiation was a small amount of an insoluble solid, which tended to coat the surface of the glass and eventually reduce the efficiency of the irradiation. At higher pD (>9), the amount of this material increased. The NMR spectrum of the solution also showed significant peaks from another mida complex, formulated as the isomer of $Pt(CH_3)_2(OD)(mida\text{-}N,O,O')^-$ with N coordinated trans to OD^- (**12a**), formed by replacement of bromide by hydroxide. If irradiation was continued when very little of the original complex **9a** remained, the amount of hydroxo complex continued to grow. Since we know (see below) that irradiation converts $Pt(CH_3)_2(OH)(mida)^-$ (isomer **6a**, with N trans to methyl) only very inefficiently to isomer **12a**, the major route to **12a** must be by photoassisted reaction of $Pt(CH_3)_2Br(mida)$ (isomer **11a**) with hydroxide, once **11a** has formed by isomerization of **9a**. Acidification of a D_2O solution of **12a** with D_2SO_4 caused ^1H NMR peaks to shift, as $Pt(CH_3)_2(D_2O)(mida\text{-}N,O,O')$ (isomer **13a**) was formed.

In a similar way, irradiation of $Pt(CH_3)_2Br(ida\text{-}N,O,O')^-$ (N trans to methyl) (**9b**) gave the isomer, **11b**, with N trans to Br. To determine whether these reactions involved interchange between free ligand and ligand originally coordinated in **9**, a solution of the complex $Pt(CH_3)_2Br(mida)^-$ (**9a**) was irradiated in the presence of an excess of free iminodiacetate. Only $Pt(CH_3)_2Br(mida)^-$ (**11a**) was formed, with no detectable iminodiacetate complex present. In a parallel experiment, $Pt(CH_3)_2Br(ida)^-$ (**9b**) was irradiated in the presence of an excess of free (methylimino)diacetate, to give only $Pt(CH_3)_2Br(ida)^-$ (**11b**). If free ligand were involved in the reaction, at least one of these experiments (depending on any thermodynamic preference for one ligand over the other) would have caused some interchange of the ligands.

Irradiation of a solution of $Pt(CH_3)_2(H_2O)(L)$ (**8**) with the mercury lamp did cause some isomerization to **13**, but much less efficiently than for the bromo analogue, with the time required being approximately 6 times longer under comparable conditions. Charge-transfer bands for the aqua complexes occur at higher energies than for the bromo complexes. Compared with the isomerization reaction, decomposition was also more noticeable. No attempt was made to isolate the products of these reactions, **13a,b**.

Thermal Isomerization Reactions. We have previously shown that some isomerization reactions of dimethylplatinum(IV) glycinate complexes that involve migration of glycinate nitrogen from a labile to an inert site can be achieved by heating.[14] To compare, qualitatively, the efficiency of thermal isomerization with the photoisomerization discussed above, a solution of $Pt(CH_3)_2Br(mida)^-$ (**9a**) was heated at 95 °C in D_2O at pD 9 in the presence of excess free ligand for 15 h. During this time, only a small amount of decomposition occurred. The ^1H NMR spectrum of the resultant solution showed predominantly peaks due to unchanged **9a**, with only traces of **11a** present. Similarly, heating at 95 °C of $Pt(CH_3)_2(D_2O)(mida)$ (**6a**) with excess $midaH_2$ at pD 2.5 gave only traces of isomer **13a**.

Heating solutions of $Pt(CH_3)_2Br(mida)^-$ (N trans to methyl, **9a**) at pD 9, in the dark, did not cause loss of bromide. Heating (95 °C) the other isomer, with N trans to bromide (**11a**), for 10 h at pD 9 did cause some replacement of bromide by hydroxide, to give $Pt(CH_3)_2(OD)(mida)^-$ (**12a**). The enhanced reactivity of the Pt–Br bond in **11a** over that in **9a** may be explained in terms of the greater trans effect of N donors compared with O donors.

Similar differences have been observed with isomers of Pt$(CH_3)_2Br(gly)_2^-$.[14]

Discussion

Many platinum(IV) halo complexes are photolabilized.[23] The proposed mechanisms involve direct heterolysis of a platinum(IV)–ligand bond. The reaction occurs from the lowest energy ligand field triplet excited state, which is reached by radiationless processes from the various ligand to metal charge-transfer excited states. This triplet state must involve electronic population of an "e_g" type orbital having antibonding character with respect to the metal–ligand σ bond.[23] We have no evidence for the mechanism of the reaction in our complexes, but in the discussion that follows, we will assume that it also proceeds through a triplet excited state. Since our complexes have much lower symmetry than octahedral, the two "e_g" type orbitals, which we shall label $(d_{z^2})^*$ and $(d_{x^2-y^2})^*$ will differ in energy. Furthermore, since methyl ligands have a high ligand field[24] and lie in the *xy* plane of the molecule, the $(d_{x^2-y^2})^*$ orbital will be higher in energy than $(d_{z^2})^*$. The lowest energy triplet state would therefore be expected to be that in which the $(d_{z^2})^*$ orbital is populated. Occupancy of this antibonding orbital would weaken all the platinum–ligand bonds, but especially those along the *z* (Br–Pt–O) axis. Weakening or breaking of the Pt–O bond in **9** allows migration of nitrogen to this coordination site. This reaction is unusual among photochemical reactions of Pt(IV) complexes, in that it is intramolecular. Side reactions at high pH, in which hydroxide replaces bromide, occur because the Pt–Br bond is also weakened. The reverse reaction, in which bromide reacts with $Pt(CH_3)_2(OH)(mida)^-$ (**6a**), occurs only to a small extent on prolonged irradiation.

If the rule applies that the most stable isomer thermodynamically is the one in which ligands with the strongest trans influence are trans to ligands with the weakest trans influence,[25] then isomer **11**, in which the two weakest ligands (carboxyl) are trans to the two strongest (methyl), will be more stable than **9**, with one N atom trans to methyl. This would explain why the conversion of **9** into **11** is irreversible.

The photoisomerization reactions of dimethylbromoplatinum(IV) complexes are of considerable synthetic utility. Combined with the kinetic effect provided by the high trans effect of the methyl ligands, they give us a fine control over the geometry of complexes with a wide variety of ligands. Mechanisms of the photochemical reactions are currently under investigation.

Acknowledgment. We thank the Australian Research Council for financial support. J.A.S., is grateful for the award of an Australian Postgraduate Research Award. We thank Dr. R. V. Tasker for carrying out some of the early experimental work.

Supplementary Material Available: Table SI, listing microanalytical data, and Tables SII and SIII, listing full NMR data (4 pages). Ordering information is given on any current masthead page.

---

(23) Ford, P. C.; Peterson, J. D.; Hintze, R. E. *Coord. Chem. Rev.* **1974**, *14*, 67.

(24) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 772.

(25) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275.

Contribution from the Department of Chemistry,
University of California at San Diego, La Jolla, California 92093

Pentacoordinate Zinc: Synthesis and Structures of Bis[1-(methylthio)-*cis*-stilbene-2-thiolato]zinc and of Its Adducts with Mono- and Bidentate Nitrogen Bases

Cheng Zhang, R. Chadha, H. K. Reddy, and G. N. Schrauzer*

Received October 2, 1990

1-(Methylthio)-*cis*-stilbene-2-thiol, $Ph(SCH_3)C{=}C(SH)Ph$, forms a dimeric μ-S-bridged zinc complex of composition $Zn_2[(CH_3)S_2C_2Ph_2]_4$, containing equivalent pentacoordinate Zn(II) ions in a trigonal-bipyramidal ligand environment; Zn–S bond lengths vary from 2.270 (3) to 2.712 (3) Å (2.46 Å average), as determined by single-crystal X-ray analysis. It reacts with 4-(dimethylamino)pyridine to yield a monomeric adduct in which Zn(II) is also pentacoordinate and the coordination geometry is distorted square-pyramidal with Zn–N and average Zn–S bond lengths of 2.069 (10) and 2.48 (25) Å. In the 2,2′-bipyridine (bpy) adduct, the zinc atom is pentacoordinate as well, although one coordinate $Zn{-}S(CH_3)$ bond is weak. The bpy ligand is symmetrically coordinated to zinc, with mean Zn–N bond distances of 2.097 (10) Å. One sulfur ligand is asymmetrically bidentate with one normal Zn–S bond of 2.292 (3) Å; the coordinative $Zn{-}S(CH_3)$ bond of 3.124 (3) Å is long but still shorter than the sum of the van der Waals radii. The other sulfur ligand is monodentate, the Zn–S bond length is 2.275 (3) Å, and the $-S-CH_3$ group is in a noninteractive position. The nitrogen ligands exchange with free ligands in solution, as evidenced by variable-temperature ^1H NMR measurements. The preferred adoption by Zn(II) of pentacoordinated structures under conditions where tetra- and hexacoordination are possible with identical probabilities suggests that pentacoordination is energetically favored and may be important in biological systems.

Complexes of zinc with S_4, S_3N, or S_2N_2 ligand cores are of interest as structural models of the immediate ligand environment of zinc in DNA-binding proteins and certain zinc-containing enzymes. While zinc is usually assumed to be tetracoordinate and this is probably true for the resting state of the biological systems, this need not necesarily be the case for their functional states, where the possibility exists that zinc adopts penta-, tri-, and perhaps even hexacoordinated structures. For example, a reactive intermediate with pentacoordinated zinc has been proposed in the reversible hydration of CO_2 by carbonic anhydrase[1] and in liver alcohol dehydrogenase.[2] Pentacoordinated complexes of zinc are known but are relatively rare. A 1983 survey[3] listed 33 structurally characterized examples among 379 mostly tetracoordinated entries. Tricoordination is probably favored in anionic complexes, as evidenced by the recent[4] characterization of the trigonal-planar anion $Zn(SR)_3^-$, where R = 2,3,5,6-Me_4C_6H, while hexacoordinated structures could be expected to occur preferentially in cationic complexes; one example is the recently reported Zn(II) complex of 1,4,7-trithiacyclononane.[5]

---

(1) (a) Gupta, R. K.; Pesando, J. M. *J. Biol. Chem.* **1975**, *250*, 2630. (b) Kannan, K. K.; Pelef, M.; Fridberg, K.; Cid-Dresner, M.; Lougren, S. *FEBS Lett.* **1977**, *73*, 115.

(2) Dworschach, R. T.; Plapp, B. V. *Biochemistry* **1977**, *16*, 2716.

(3) Auf der Heyde, T. P. E.; Nassimbeni, L. R. *Acta Crystallogr.* **1984**, *B40*, 582.

(4) Gruff, E. S.; Koch, S. A. *J. Am. Chem. Soc.* **1989**, *111*, 8762.

0020-1669/91/1330-3865$02.50/0 © 1991 American Chemical Society