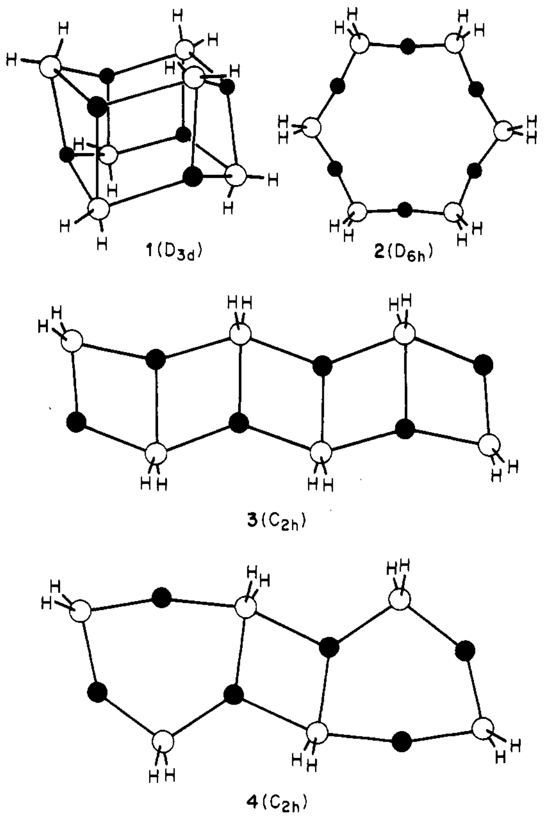

Figure 1. Structures considered in this study. Dark circles represent Li and open circles represent N. The Li–N frameworks in the figures have been computer generated and are true to scale based on the optimized 3-21G geometries.

perform similar calculations on the hexamer of $LiN{=}CH_2$ to investigate this aspect further.

CSW have now suggested that a 3-dimensional cluster structure such as **1** is unlikely to be the ground state of substituted amide hexamers and that they "will favor structures based on (LiN) rings, with possible lateral association of these rings". In our previous work, we had reported only preliminary investigations of such structures. Since then, we have finished more accurate calculations on such structures which show convincingly that **1** is significantly more stable than such structures, at least in the case of $(LiNH_2)_6$.

We now report the results on two such structures based on lateral association of planar $(LiN)_n$ rings, viz. (i) a ladder[12] or "fence"[13] structure **3** with C_{2h} symmetry which is a lateral association of cyclic dimers[14] and (ii) a structure **4**, also with C_{2h} symmetry, consisting of two cyclic trimers[14] associated laterally. Since **1** can be considered as a 3-dimensional association of two trimers, the 2-dimensional association as in **4** illustrates an important contrast. The geometries of both **3** and **4** were completely optimized with the valence-double ζ 3-21G basis set.[15] In addition, 6-31G calculations,[9] which have been previously shown to be reliable for the prediction of relative energies of $LiNH_2$ clusters,[1,5] were performed. Though both **3** and **4** are slightly more stable than the D_{6h} form **2**, they are *significantly less stable* than the D_{3d} cluster structure **1**, lying 15 and 18 kcal/mol higher in energy, respectively, at the 6-31G level. On the basis of our previous experience[1,5] with $(LiNH_2)_4$ and $(LiNH_2)_6$, we estimate that the uncertainity in the calculated relative energies is less than 5 kcal/mol.

CSW have also stated that steric reasons will prevent the formation of structures such as **1** in the case of substituted amides. Though we have not yet performed any calculations on substituted amides, inspection of the geometry of **1** indicates that the orientation of the hydrogens is such that there may not be large steric effects if the hydrogens are replaced by alkyl groups. In any case, 3-dimensional cluster structures are known experimentally[16] even in cases such as $[LiSi(CH_3)_3]_6$, which have even larger steric effects. Further calculations on the hexamers of substituted amides may be necessary to resolve this matter further.

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Proton NMR Studies of Paramagnetic Polypyridyl μ-Oxo Complexes of Ruthenium(III) and Their Diamagnetic Ruthenium(II) Precursors

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The use of nuclear magnetic resonance spectral techniques as a structural probe for diamagnetic $(d\pi)^6$ polypyridyl complexes has been extensive.[1] As the synthetic chemistry of these complexes has evolved, important structural and dynamic problems have arisen involving oxidation states with unpaired spins. X-ray crystallographic and, in some instances, EPR methods have been utilized successfully for the determination of solid-phase molecular and electronic structures, but questions of stereochemistry, fluxional behavior, or substitution dynamics in solution remain to be addressed through the application of paramagnetic NMR techniques.[2]

High-valent oxo complexes of Ru have proven to be efficient stoichiometric and/or catalytic oxidants in a series of organic and

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Table I. Chemical Shifts of Bipyridyl Protons in Complexes of the Type *cis*-$[b_2Ru^{II}(OH_2)_2]^{2+}$ [a,b]

	protons[c]							
complex	3	3′	4	4′	5	5′	6	6′
cis-$[(bpy)_2Ru^{II}(OH_2)_2]^{2+}$	8.59 (d)	8.38 (d)	7.90 (t)	8.26 (t)	7.11 (t)	7.79 (t)	7.74 (d)	9.38 (d)
cis-$[(5,5'\text{-dmbp})_2Ru^{II}(OH_2)_2]^{2+}$	8.40 (d)	8.20 (d)	7.47 (d)	8.06 (d)	CH_3 2.63	CH_3 2.07	7.60 (s)	9.17 (s)
cis-$[(4,4'\text{-dmbp})_2Ru^{II}(OH_2)_2]^{2+}$	8.35 (s)	8.13 (s)	CH_3 2.67	CH_3 2.38	6.89 (d)	7.66 (d)	7.45 (d)	9.09 (d)

[a] In $D_2O/\sim0.1$ M D_2SO_4 and referenced to DSS. [b] (bpy) is 2,2′-bipyridine; (5,5′-dmbp) is 5,5′-dimethyl-2,2′-bipyridine; (4,4′-dmbp) is 4,4′-dimethyl-2,2′-bipyridine. [c] Chemical shifts are in ppm; peak multiplicities are in parentheses; see text for description of primed notation.

inorganic oxidations.[3,4] Especially notable in this regard is the catalytic oxidation of water by the Ru(V)–Ru(V) form of the μ-oxo ion $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ (bpy is 2,2′-bipyridine) and its derivatives.[3c,5] In this paper we present the results of paramagnetic ^1H NMR spectral studies on some polypyridyl complexes containing the Ru^{III}–O–Ru^{III} unit and their diamagnetic Ru(II) precursors. Our results allow us to assign the proton spectra of the oxo-bridged complexes and to demonstrate that paramagnetic NMR techniques can provide a valuable probe for unraveling the underlying substitutional chemistry.

Experimental Section

Materials. All NMR grade deuterated solvents were purchased from Aldrich Chemical Company.

Preparations. The syntheses of *cis*-$[Ru^{II}(bpy)_2(OH_2)_2]^{2+}$,[6a] *cis*-$[Ru^{II}(4,4'\text{-dmbp})_2(OH_2)_2]^{2+}$,[6a] *cis*-$[Ru^{II}(5,5'\text{-dmbp})_2(OH_2)_2]^{2+}$,[6a] *cis*-$Ru^{II}(5,5'\text{-dmbp})_2Cl_2\cdot H_2O$,[6a] $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2](ClO_4)_4$,[5a] and $[(bpy)_2(py)Ru^{III}ORu^{III}(py)(bpy)_2](ClO_4)_4$[6b] have been described previously. 4,4′-dmbp is 4,4′-dimethyl-2,2′-bipyridine; 5,5′-dmbp is 5,5′-dimethyl-2,2′-dipyridine; py is pyridine.

$[(5,5'\text{-dmbp})_2(OH_2)Ru^{III}ORu^{III}(OH_2)(5,5'\text{-dmbp})_2](ClO_4)_4\cdot H_2O$. To 30 mL of distilled H_2O was added 1.057 g (1.89 mmol) of *cis*-$[Ru^{II}(5,5'\text{-dmbp})Cl_2\cdot H_2O$. The solution was kept in the dark and heated to reflux with stirring at which time 0.804 g (4.74 mmol) of $AgNO_3$ was added. The absence of light helps minimize cis → trans isomerization[7] of *cis*-$[Ru^{II}(5,5'\text{-dmbp})_2(OH_2)_2]^{2+}$ and subsequent formation of the cis–trans–cis bis(μ-oxo) complex Ru(III)–Ru(IV)–Ru(III).[8] The solution was again heated at reflux for 30 min after which time the AgCl precipitate was collected by filtration. The filtrate was heated at reflux for an additional 30 min and allowed to cool to room temperature. A saturated $NaClO_4$(aq) solution (5 mL) was added to the solution, which was allowed to stand for 15 min. The deep blue-black microcrystalline product was collected on a medium frit and washed with 1 × 5 mL portions of cold 0.1 M $HClO_4$(aq). The crude product was recrystallized by dissolving in warm H_2O and adding saturated $NaClO_4$(aq) until precipitation just began. The microcrystalline product was washed with 1 × 5 mL portions of cold H_2O and dried in vacuo. Yield after recrystallization: 0.4m g, 38%. Anal. Calcd for $Ru_2C_{48}H_{54}O_{20}N_8Cl_4$: C, 40.96; H, 3.84; N, 7.96; Cl, 10.10. Found: C, 40.38; H, 3.96; N, 8.03; Cl, 10.60.

Table II. Narrow-Band Decoupling of the ^1H NMR Spectrum of the μ-Oxo Complex $[(bpy)_2(OH_2)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2]^{4+}$ in D_2O[a]

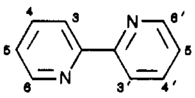
chem shift, ppm vs DSC		chem shift, ppm vs DSC	
irradiated peak	decoupled peak	irradiated peak	decoupled peak
20.4 (d)	10.4 (t → d)	2.9 (t)	9.9 (d → s)
14.1 (d)	−15.4 (t → d)		9.3 (d → s)
12.3 (s)	...	0.3 (d)	10.4 (t → d)
10.4 (t)	0.3 (d → s)	−1.3 (t)	9.6 (d → s)
	20.4 (d → s)		9.2 (d → s)
10.2 (d)	−15.4 (t → d)	−6.7 (s)	...
9.9 (d)	2.9 (t → d)	−15.4 (t)	10.2 (d → s)
9.6 (d)	−1.3 (t → d)		14.1 (d → s)
9.3 (d)	2.9 (t → d)	−21.9 (s)	...
9.2 (d)	−1.3 (t → d)		

[a] Spectra recorded at 20 °C. Letters in parentheses refer to peak multiplicities.

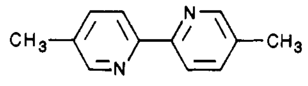
$[(bpy)_2(py\text{-}d_5)Ru^{III}ORu^{III}(py\text{-}d_5)(bpy)_2](ClO_4)_4$. The perdeuteriated pyridyl complex was prepared by using the previously reported synthesis for the protio analogue.[6b]

Results and Discussion

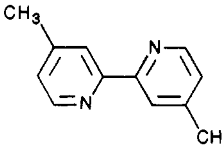
Properties of the Precursor Complexes. The water oxidation catalyst $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$ is prepared by oxidation of *cis*-$[Ru^{II}(bpy)_2(OH_2)_2]^{2+}$. In Table I are shown the chemical shift values for the 2,2′-bipyridine protons of *cis*-$[Ru^{II}(bpy)_2(OH_2)_2]^{2+}$. Assignments were made based on comparison of the spectrum with the spectra of the independently synthesized (5,5-dmbp) and (4,4′-dmbp) diaqua analogues. The assignments are consistent with those made previously for *cis*-$[Ru^{II}(bpy)_2(py)_2]^{2+}$ by Constable and Seddon.[11] The dramatic chemical shift difference between the 6 and 6′ protons (~1.6 ppm) can be rationalized by examining molecular models which show that the proton in the 6-position lies in close proximity to the ring currents of the second bipyridine ring and is thus shielded relative to the 6′ proton. The primed notation refers to those two of the pyridine rings of the bipyridine ligands that are trans to one another. We have no basis for assigning the methyl resonances in the methyl-substituted derivatives to the primed or unprimed rings.



bpy



5,5′-dmbp



4,4′-dmbp

NMR Spectral Properties of μ-Oxo Ru(III) Complexes. The μ-oxo complex $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$, prepared by oxidation of the diaqua monomer, is paramagnetic, at least in the solid state. The room-temperature magnetic moment is 1.604 μ_B/dimer unit for the ClO_4^- salt as determined by the Faraday method. The paramagnetism of the complex persists in solution and gives rise to the dramatically shifted spectrum shown

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Table III. Chemical Shifts[a,b] in the Paramagnetic ^1H NMR Spectra of μ-Oxo Complexes of the Type $Ru^{III}(O)Ru^{III}$

	chem shift, ppm vs DSC		
protons	$[(bpy)_2(OH_2)Ru^{III}]_2O^{4+}$	$[(5,5'\text{-dmbp})_2(OH_2)Ru^{III}]_2O^{4+}$	$[(bpy)_2(py)Ru^{III}]_2O^{4+}$
3 (3′)	14.1, 9–10 (2), 0.3	14.2, 9.2 (2), −2.6	13.9, 9–12 (2), −0.1
4 (4′)	10.4, 2.9, −1.3, −15.4	11.2, −1.5, −3.4, −19.8	9–12 (1), 3.0, −0.6, −15.4
5 (5′)	20.4, 10.2, 9–10 (2)		21.9, 9–12 (3)
6 (6′)	12.3, −6.7, −21.9	13.0, −9.2, −26.8	13.4, 3.4, −3.2, −21.1
CH_3 groups		8.8, 3.0, 0.4, −8.8	
pyridine			12.9 (2), 6.4, 5.4 (2)

[a] Spectra recorded at 20 °C in D_2O. [b] In cases where a range is given (i.e. 9–10), several resonances are present and an unambiguous distinction between the 3 (3′) and 5 (5′) assignments cannot be made. Numbers in parentheses are the number of the indicated protons present in the range given.

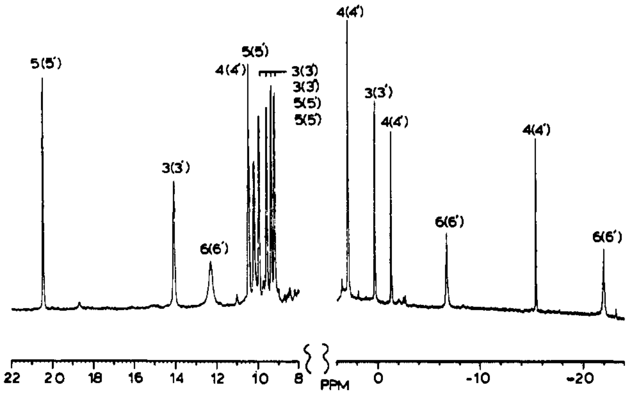

Figure 1. ^1H NMR spectrum of $[(bpy)_2(OH_2)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2](ClO_4)_4$ in D_2O relative to sodium 2,2′-dimethylsilapentane-5-sulfonate (DSS).

in Figure 1. Presumably, contributions to the shifts and broadening exist from both dipolar and Fermi contact shift terms which is typically the case for paramagnetic transition-metal complexes with unpaired electrons in the dπ levels.[9]

In an electronic sense the situation in the μ-oxo ion is made even more complex by electronic coupling between the Ru(III) sites through the μ-oxo bridge. Compared with monomeric complexes of Ru(III), the effect of coupling on the spin relaxation dynamics is significant, which allowed us to perform narrow-band decoupling experiments on $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$, the results of which are summarized in Table II. This capability, combined with the spectrum of the (5,5′-dmbp) analogue, allowed us to design the very complex spectrum. From the previously published X-ray crystal structure of $[(bpy)_2(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$, a 2-fold axis of symmetry exists, which lies through the μ-oxo bridge.[5a] If the 2-fold symmetry were maintained in solution, 16 resonances should appear from the nonequivalent protons of the two bipyridyl rings chelated to ruthenium. The comparison of relative line widths was useful for preliminary analysis of the spectrum in Figure 1.

On the basis of observations made previously by Drago and Simone, the broadest resonances were assigned to the 6 (6′) protons.[10] The assignments of the 5 (5′) protons followed straightforwardly from the spectrum of the (5,5′-dmbp) analogue. The remaining four pseudotriplets can therefore be unambiguously assigned to the 4 (4′) protons and results obtained from the decoupling experiments complete the 3 (3′) assignments and corroborate the assumptions used above. In both the spectrum of the bpy dimer and its (5,5′-dmbp) analogue, we were unable to locate the fourth 6 (6′) proton and, based on its chemical shift of 3.39 ppm in the py–py analogue assume that it lies beneath the solvent peak.

Assignments of the ^1H NMR resonances for both of the μ-oxo aqua complexes and for $[(bpy)_2(py)Ru^{III}ORu^{III}(py)(bpy)_2]^{4+}$ are summarized in Table III. The assignments for the bis-pyridyl complex are of relevance in the context of the substitution studies to be discussed below. The pyridyl resonances of the μ-oxo dimer were assigned based on comparisons with the spectrum of $[(bpy)_2(d_5\text{-py})Ru^{III}ORu^{III}(d_5\text{-py})(bpy)_2]^{4+}$.

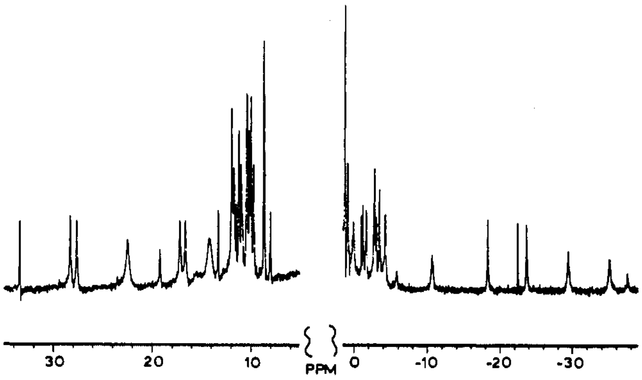

Figure 2. ^1H NMR spectrum obtained upon dissolving $[(bpy)_2(OH_2)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2](ClO_4)_4$ in CD_3CN. The spectrum is consistent with the formation of the unsymmetrical μ-oxo complex $[(bpy)_2(OH_2)Ru^{III}(O)Ru^{III}(CD_3CN)(bpy)_2]^{4+}$.

Applications. Substitution in the μ-Oxo Complexes. With the ^1H NMR assignments in hand it is possible to use NMR to follow the substitution-based chemistry of the μ-oxo complex. Addition of $[(bpy)_2(H_2O)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2]^{4+}$ to CD_3CN rapidly leads to the formation of the unsymmetrical complex $[(bpy)_2(CD_3CN)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2]^{4+}$ as can be seen in Figure 2. The concomitant changes in the ^1H NMR spectrum are profound in that the loss of symmetry across the μ-oxo bridge increases the number of resonances from 16 to 32. Substitution at the initial site occurs on the timescale of mixing and data acquisition ($t_{1/2} < 10$ min). Substitution at the second site with the loss of another molecule of H_2O is far slower. Formation of $[(bpy)_2(CD_3CN)Ru^{III}(O)Ru^{III}(NCCD_3)(bpy)_2]^{4+}$ is not complete even after several hours.

When oxidized to $[(bpy)_2(O)Ru^{V}(O)Ru^{V}(O)(bpy)_2]^{4+}$, the μ-oxo system becomes a catalyst for the oxidation of Cl^- to Cl_2 but the catalytic ability of the system is lost following anation of the Ru(III)–Ru(III) and/or Ru(IV)–Ru(III) μ-oxo ions by Cl^-.[11] In a D_2O solution containing 1.0 M Cl^- rapid initial anation ($t_{1/2} < 10$ min) occurred as shown by the loss of symmetry and increase in the number of resonances consistent with the formation of the unsymmetrical ion $[(bpy)_2(Cl)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2]^{3+}$.

The substitution rate for the μ-oxo py–py complex $[(bpy)_2(py)Ru^{III}(O)Ru^{III}(py)(bpy)_2]^{4+}$ is substantially slower under similar conditions, $t_{1/2} \sim 9.5$ h for substitution of the first pyridyl group in CD_3CN.

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Registry No. $[(5,5'\text{-dmbp})_2(OH_2)Ru^{III}ORu^{III}(OH_2)(5,5'\text{-dmbp})_2](ClO_4)_4$, 116563-72-5; *cis*-$[Ru^{II}(5,5'\text{-dmpb})Cl_2]$, 115890-21-6; $[(bpy)_2(OH_2)Ru^{III}]_2O^{4+}$, 96364-19-1; $[(bpy)_2(py)Ru^{III}]_2O^{4+}$, 107985-02-4; *cis*-$[(bpy)_2Ru^{II}(OH_2)_2]^{2+}$, 72174-09-5; *cis*-$[(5,5'\text{-dmbp})_2Ru^{II}(OH_2)_2]^{2+}$, 116563-73-6; *cis*-$[(4,4'\text{-dmbp})_2Ru^{II}(OH_2)_2]^{2+}$, 116563-74-7; $[(bpy)_2(CD_3CN)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2]^{4+}$, 116563-75-8; $[(bpy)_2(CD_3CN)Ru^{III}(O)Ru^{III}(NCCD_3)(bpy)_2]^{4+}$, 116563-76-9; $[(bpy)_2(Cl)Ru^{III}(O)Ru^{III}(OH_2)(bpy)_2]^{3+}$, 116563-77-0.

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Reaction between Ethylenediamine and Acetone on a Platinum(II) Complex. Crystal Structure of $[PtCl(en)(PBu_3)][PtCl(ien)(PBu_3)]Cl_2\cdot CH_3COCH_3$

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Nickel(II) and copper(II) complexes with imino derivatives of ethylenediamine as ligands have been known for a long time.[2] They all have been prepared by a base-catalyzed reaction between an ethylenediamine complex and acetone. We have accidentally discovered a platinum(II) complex bearing one *N*-isopropylideneethylenediamine ligand, where the imine forms in the other way: by a reaction of coordinated acetone with free ethylenediamine. We have tried to use *sym-trans*-$[Pt_2Cl_4(PBu_3)_2]$ (**1**) (Bu = *n*-butyl) to synthesize $[PtCl(en)(PBu_3)]Cl$ (**2**). While the reaction of **1** with 2 equiv of ethylenediamine in ether or dichloromethane gives quantitatively **2**,[3] in acetone, a crystalline compound forms, which we have identified as $[PtCl(en)(PBu_3)][PtCl(ien)(PBu_3)]Cl_2\cdot CH_3COCH_3$ (ien = *N*-isopropylideneethylenediamine) (**2**(**3**)·CH_3COCH_3) (Scheme I). We have then tried to prepare **3** from **2** by dissolving **2** in acetone, alone and in presence of 1 equiv of triethylamine. In either case, no NMR signals due to **3** could be detected. Thus, formation of **3** via **2** by a base-catalyzed reaction of coordinated ethylenediamine with free acetone is ruled out. It is known that bridged binuclear complexes *sym-trans*-$[Pt_2Cl_4(PR_3)_2]$ undergo in acetone a solvolysis, yielding the labile complex *trans*-$[PtCl_2(acetone)(PR_3)]$.[4] The latter can react with ethylenediamine either in a substitution reaction leading in our case finally to **2** or in a condensation reaction between one amino group of ethylenediamine and the acetone ligand, which is polarized by the coordination on platinum. This condensation yields *N*-isopropylideneethylenediamine, which can be stabilized by chelate bonding in complex **3** (Scheme I). Crystallization of the mixed compound **2**(**3**)·CH_3COCH_3 obviously prevents **3** from being hydrolyzed to **2** and acetone; left in the initial solution at ambient temperature, the crystals of **2**(**3**)·CH_3COCH_3 start to dissolve after 5 days, and in the final solution, **2** is the only species detectable by ^{31}P NMR spectroscopy. We are currently trying to identify the (at least four) intermediate species that appear in the ^{31}P NMR spectrum during the reaction of **1** with ethylenediamine in acetone, in order to elucidate the exact mechanism. We wish to communicate here the synthesis and characterization of the mixed compound **2**(**3**)·CH_3COCH_3, including an X-ray structure determination.

Table I. Details of the X-ray Analysis of **2**(**3**)·CH_3COCH_3

formula	$C_{34}H_{80}Cl_4N_4OP_2Pt_2$
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	17.459 (2)
b, Å	12.107 (3)
c, Å	23.742 (3)
β, deg	92.16
V, Å^3	5015 (2)
Z	4
cryst size, mm	0.6 × 0.3 × 0.2
μ, cm^{-1}	59.3
ρ(calcd), g·cm^{-3}	1.52
temp, °C	23
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
scan method	$\omega/2\theta$
θ limits, deg	$1 \le \theta \le 20$
data collcd	$k, l \ge 0, \pm h$
no. of collcd reflcns	4981
no. of unique reflcns with $F \ge 3\sigma(F)$	2978
R	0.0450
R_w[a]	0.0528
R_{int}	0.0209

[a] $w = 1/\sum_{r=1,3} A_r T_r(x)$: $A_1 = 8.51$; $A_2 = -3.73$; $A_3 = 6.13$; T_r is the Chebyshev polynomial with $x = F_c/F_{o\,max}$.[5]

Experimental Section

sym-trans-$[Pt_2Cl_4(PBu_3)_2]$ (**1**) was purchased from Strem Chemicals. NMR spectra were recorded on a Bruker WM 250 spectrometer. References used were TMS (^1H) and external H_3PO_4 85% (^{31}P). IR spectra were recorded on a Perkin-Elmer 157 G spectrometer.

$[PtCl(en)(PBu_3)][PtCl(ien)(PBu_3)]Cl_2\cdot CH_3COCH_3$ (2(3)·CH_3COCH_3). To a stirred solution of **1** (0.05 mmol) in acetone (1.5 mL) was added dropwise a solution of ethylenediamine (0.1 mmol) in acetone (0.5 mL). From the resulting pale yellow solution, the product precipitates, upon stirring at room temperature, as colorless microcrystalline material. The yields vary between 0 (no crystallization) and 20%, depending on the intensity of stirring and the period over which ethylenediamine is added; no clear-cut dependence could be derived, though. In air, the crystals slowly lose acetone, which can be removed completely in vacuo. Anal. Calcd./found for **2**(**3**) (devoid of acetone) ($C_{31}H_{74}Cl_4N_4P_2Pt_2$): C, 33.94/33.9; H, 6.80/6.8.

X-ray Analysis. Single crystals of **2**(**3**)·CH_3COCH_3 were obtained from spun NMR tubes (o.d. 10mm) to which the solution was transferred immediately after addition of ethylenediamine. A crystal was mounted in a glass capillary on an Enraf Nonius CAD 4 diffractometer. The structure was solved by using the heavy-atom method and refined by least-squares techniques in three blocks. Some atoms of the *n*-butyl chains as well as the acetone atoms were diffuse and refined to unreasonable bond lengths and angles; thus, these groups were constrained to standard configurations. Anisotropic thermal parameters for Pt, P, and Cl were introduced; hydrogen atoms were not included. Scattering factors with anomalous dispersion correction were taken from CRYSTALS.[5] A secondary extinction correction was applied. An empirical absorption correction was made by using ψ scans with two reflections (transmission factor min/max = 1.00/1.56). Two standard reflections were measured every 2 h so that corrections for crystal decomposition could be made; their intensities decreased by 35% in the course of the experiment. The details of the data collection and refinement are given in Table I.

Results and Discussion

Crystal Structure of 2(3)·CH_3COCH_3. Atomic coordinates are listed in Table II. ORTEP drawings of the two complex ions of **2** and **3** are shown in Figure 1. Important bond distances and angles are given in Table III. The coordination around Pt is in both complexes square planar, with deviations from the least-squares planes of ≤0.08 Å. The respective Pt–P and Pt–N bond

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