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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(2) Blight, M. M.; Curtis, N. F. *J. Chem. Soc.* **1962**, 1204–1207, 3016–3020.

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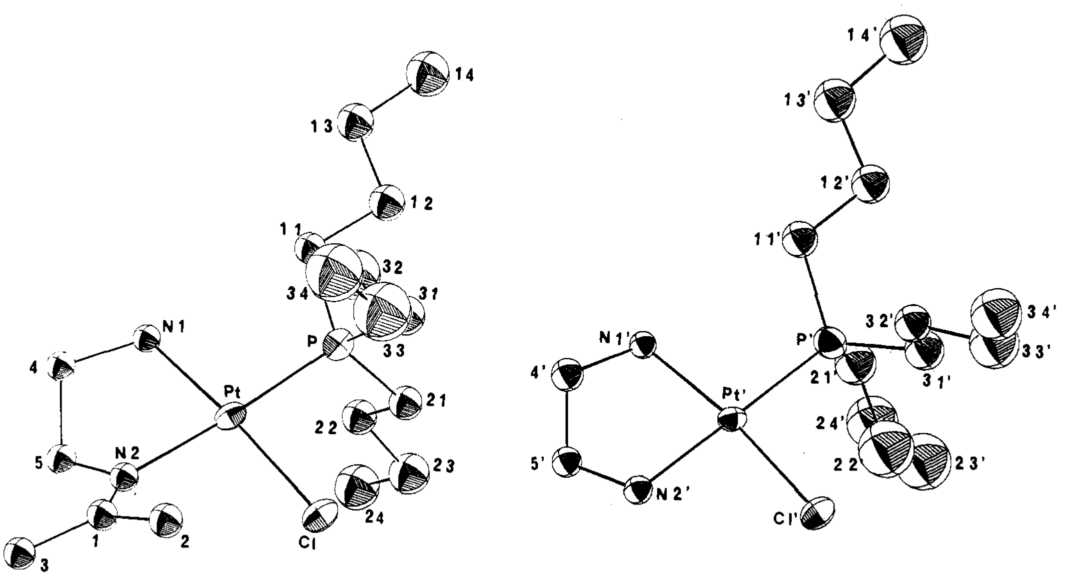
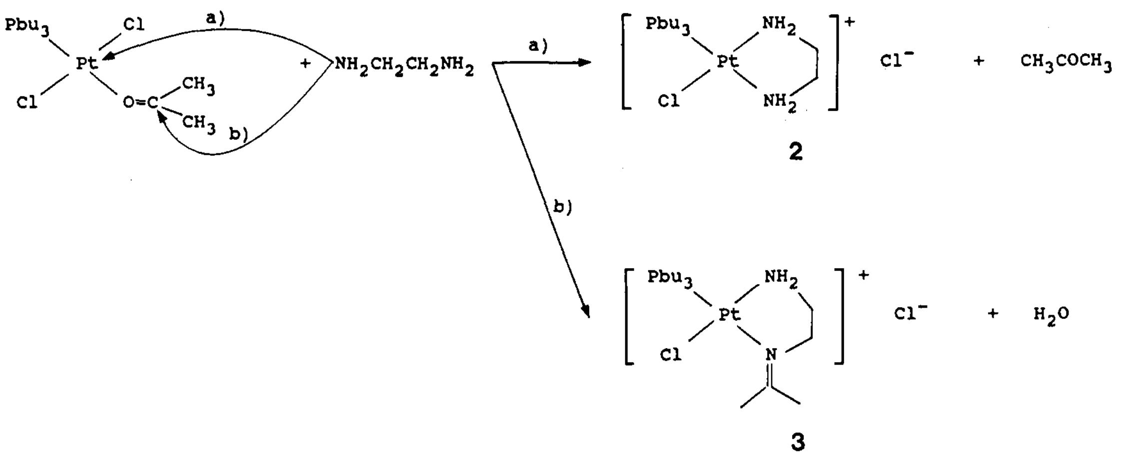


Figure 1. ORTEP drawings with the numbering schemes of the complex cations of 3 (left) and 2 (right). Carbon atoms are labeled with numbers only. 20% probability ellipsoids were used.

Scheme I



lengths of **2** and **3** do not differ within experimental error; hence, the Pt–N(amine) and Pt–N(imine) bonds have comparable strengths and trans influences. In the complex cation of **3**, the C═N group and all four vicinal atoms lie in a plane (deviations ≤0.07 Å) that is twisted by 38° against the platinum coordination plane. This arrangement, which precludes significant Pt → N π-back-bonding, probably results from the repulsion of one methyl group with the Cl ligand (Cl–C(2) distance = 3.24 Å) and from constraints of the chelate ring. The lattice is stabilized by a network of hydrogen bonds between uncoordinated chloride ions and amino groups, each Cl^- being connected to three NH_2 groups (Figure 2). There are no hydrogen bonds to the carbonyl group of acetone and no direct interactions between **2** and **3**, which would explain why the two compounds cocrystallize.

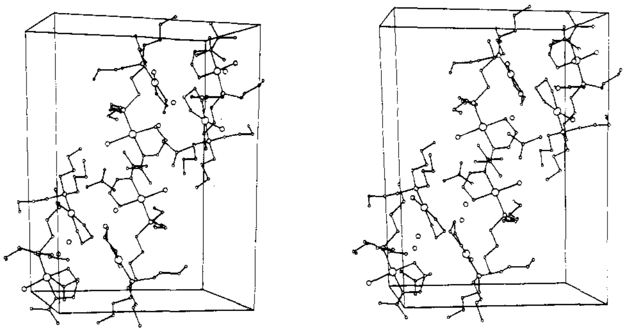


Figure 2. Stereoview of the unit cell of **2**(**3**)·CH_3COCH_3: large circles, Pt; medium circles, P, Cl; small circles, C, N, O.

NMR Spectra. The $^{31}P\{^1H\}$ NMR spectrum of **2**(**3**)·CH_3COCH_3 in D_2O is composed of two peaks of the same intensity with satellites due to ^{195}Pt; one of the two signals is identical with that of the pure compound **2**: $\delta_P = -3.2$ ppm, $J_{Pt-P} = 3240$ Hz. The second signal ($\delta_P = -5.7$ ppm, $J_{Pt-P} = 3214$ Hz) was accordingly attributed to compound **3**. The coupling constants correspond to a phosphine trans to a nitrogen ligand[6] and confirm that the trans influence of the imino group is very close to that of the amino group. The ^1H NMR spectrum of **2**(**3**) (dried in vacuo) in D_2O shows two unresolved peaks at 2.16 and 2.42 ppm that are absent in the spectrum of **2** and were attributed to the isopropylidene protons.[7] The methylene protons adjacent to the imino group give rise to a broad absorption centered at 3.7 ppm while a multiplet due to those adjacent to NH_2 appears at 2.7–2.8 ppm. The *n*-butyl protons give rise to four multiplets centered at 0.9, 1.5, 1.6, and 1.8 ppm, respectively. Integration of all signals is in agreement with the formula **2**(**3**). When the D_2O solution of **2**(**3**) is left at ambient temperature, the NMR signals due to **3** decrease slowly ($\tau_{1/2} = 170$ h) in favor of those of **2**, and in the proton spectrum, a singlet appears at 2.22 ppm, indicating the release of acetone in the course of the hydrolysis of **3** to **2**.

The IR spectrum (KBr pellets) of **2** reveals a medium absorption at 1591 cm^{-1} due to NH_2 bending modes. The spectrum of **2**(**3**)

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(7) Staab, H. A.; Vögtle, F.; Mannschreck, A. *Tetrahedron Lett.* **1965**, 697–702.

Table II. Atomic and Thermal Parameters for [PtCl(en)(PBu$_3$)][PtCl(ien)(PBu$_3$)]Cl$_2$·CH$_3$COCH$_3$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(iso)
Pt	−0.04332 (3)	0.09764 (5)	0.11925 (3)	0.0815[a]
Cl	−0.1632 (3)	0.0469 (5)	0.0831 (2)	0.1183[a]
P	−0.0864 (3)	0.0660 (4)	0.2048 (2)	0.1011[a]
N(1)	0.0679 (6)	0.1249 (9)	0.1480 (5)	0.079 (3)
N(2)	0.0049 (7)	0.130 (1)	0.0423 (5)	0.085 (3)
C(1)	−0.0206 (9)	0.183 (1)	−0.0028 (7)	0.098 (5)
C(2)	−0.102 (1)	0.232 (2)	−0.0029 (8)	0.118 (6)
C(3)	0.026 (1)	0.198 (1)	−0.0540 (7)	0.105 (5)
C(4)	0.1176 (9)	0.154 (1)	0.0999 (6)	0.090 (4)
C(5)	0.0864 (9)	0.095 (1)	0.0476 (7)	0.094 (5)
C(11)	−0.0128 (8)	0.088 (1)	0.2613 (6)	0.104 (5)
C(12)	−0.043 (1)	0.059 (2)	0.3200 (7)	0.134 (7)
C(13)	0.022 (1)	0.084 (2)	0.3637 (8)	0.141 (7)
C(14)	−0.001 (2)	0.048 (3)	0.4235 (9)	0.20 (1)
C(21)	−0.1228 (9)	−0.078 (1)	0.2139 (8)	0.116 (6)
C(22)	−0.0553 (9)	−0.158 (1)	0.2119 (9)	0.126 (6)
C(23)	−0.084 (1)	−0.278 (2)	0.212 (1)	0.172 (9)
C(24)	−0.013 (2)	−0.354 (2)	0.208 (1)	0.21 (1)
C(31)	−0.168 (1)	0.155 (2)	0.221 (1)	0.157 (8)
C(32)	−0.148 (2)	0.276 (2)	0.209 (2)	0.26 (2)
C(33)	−0.216 (2)	0.327 (3)	0.176 (2)	0.35 (2)
C(34)	−0.198 (3)	0.448 (3)	0.164 (2)	0.34 (3)
Pt′	0.32487 (4)	0.14951 (5)	0.17590 (3)	0.0812[a]
Cl′	0.3689 (4)	0.3154 (4)	0.1445 (3)	0.1382[a]
P′	0.3727 (3)	0.0599 (5)	0.1032 (2)	0.1223[a]
N′(1)	0.2830 (6)	0.010 (1)	0.2143 (5)	0.080 (3)
N′(2)	0.2810 (7)	0.230 (1)	0.2459 (5)	0.091 (4)
C′(4)	0.235 (1)	0.047 (2)	0.2611 (8)	0.118 (6)
C′(5)	0.269 (1)	0.143 (1)	0.2893 (7)	0.101 (5)
C′(11)	0.326 (1)	−0.074 (1)	0.0908 (8)	0.143 (7)
C′(12)	0.352 (1)	−0.131 (2)	0.0362 (9)	0.164 (9)
C′(13)	0.315 (2)	−0.248 (2)	0.035 (1)	0.19 (1)
C′(14)	0.334 (2)	−0.304 (3)	−0.022 (1)	0.26 (2)
C′(21)	0.474 (1)	0.005 (2)	0.120 (1)	0.19 (1)
C′(22)	0.530 (2)	0.099 (3)	0.132 (2)	0.35 (3)
C′(23)	0.615 (2)	0.058 (4)	0.133 (2)	0.35 (2)
C′(24)	0.622 (2)	−0.051 (4)	0.165 (2)	0.30 (2)
C′(31)	0.382 (1)	0.137 (2)	0.0381 (8)	0.175 (9)
C′(32)	0.302 (1)	0.172 (2)	0.0165 (9)	0.151 (8)
C′(33)	0.319 (2)	0.248 (3)	−0.034 (1)	0.28 (2)
C′(34)	0.246 (2)	0.285 (4)	−0.064 (2)	0.29 (2)
Cl(2)	0.3587 (2)	0.3849 (3)	0.3436 (2)	0.0976[a]
Cl(3)	0.1077 (3)	0.3271 (4)	0.2322 (2)	0.1094[a]
O	0.091 (1)	0.409 (2)	0.014 (1)	0.27 (1)
C(6)	0.097 (1)	0.457 (3)	0.060 (1)	0.25 (2)
C(7)	0.178 (2)	0.483 (3)	0.083 (1)	0.25 (2)
C(8)	0.027 (2)	0.469 (3)	0.094 (1)	0.27 (2)

[a] Equivalent *U* values.

Table III. Selected Distances (Å) and Angles (deg) for [PtCl(en)(PBu$_3$)][PtCl(ien)(PBu$_3$)]Cl$_2$·CH$_3$COCH$_3$

Pt-Cl	2.315 (4)	Pt′-Cl′	2.286 (5)
Pt-P	2.226 (5)	Pt′-P′	2.229 (5)
Pt-N(1)	2.06 (1)	Pt′-N′(1)	2.07 (1)
Pt-N(2)	2.08 (1)	Pt′-N′(2)	2.10 (1)
C(1)-N(2)	1.31 (2)		
P-Pt-Cl	87.8 (2)	P′-Pt′-Cl′	92.0 (2)
N(1)-Pt-Cl	173.2 (3)	N′(1)-Pt′-Cl′	172.5 (4)
N(1)-Pt-P(1)	94.2 (3)	N′(1)-Pt′-P′	95.3 (4)
N(2)-Pt-Cl	96.6 (3)	N′(2)-Pt′-Cl′	89.2 (4)
N(2)-Pt-P(1)	175.7 (3)	N′(2)-Pt′-P′	178.4 (4)
N(2)-Pt-N(1)	81.5 (5)	N′(1)-Pt′-N′(2)	83.5 (5)
Pt-N(2)-C(5)	107.0 (9)	C(2)-C(1)-N(2)	118.4 (15)
Pt-N(2)-C(1)	132.2 (11)	C(3)-C(1)-N(2)	123.0 (14)
C(1)-N(2)-C(5)	120.2 (13)	C(3)-C(1)-C(2)	118.7 (15)

shows, in addition, a strong peak at 1649 cm^{-1}, identified with the C=N stretching.[8]

Imines form stable metal complexes only if the imino group is involved in a chelate ring.[9,10] It has been argued that the basic strength of the C=N bond is too low to permit the formation of stable complexes by simple coordination.[9a] Our finding of equal bond lengths for Pt-N(amine) and Pt-N(imine) in chemically equivalent environments suggests that the reactivity of imine metal complexes is not due to an inherent weakness of the M-N(imine) bond but rather to the susceptibility of the coordinated C=N group to nucleophilic attack.

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Registry No. **1**, 15282-39-0; **2**(**3**)·CH$_3$COCH$_3$, 115704-90-0; en, 107-15-3; CH$_3$COCH$_3$, 67-64-1.

Supplementary Material Available: Tables SI-SIII, listing anisotropic thermal parameters, additional bond distances and angles, and least-squares planes for **2**(**3**)·CH$_3$COCH$_3$ (3 pages); Table SIV, listing observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(10) Recently, the synthesis of some stable platinum(II) complexes involving monodentate aromatic imine ligands has been reported.[11]

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Synthesis and Characterization of a New Type of Heteropolyanion: Pentamolybdobis(*n*-propylarsonate), Having Two Types of Crystals under the Same pH Conditions in the Same Solution

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Received January 22, 1988

We wish to report the synthesis and structure of a new type of heteropolyanion, [(RAs)$_2$Mo$_5$O$_{21}$]$^{4-}$. Although salts of the anions [(RP)$_2$Mo$_5$O$_{21}$]$^{4-}$ and [(RAs)$_2$Mo$_6$O$_{24}$]$^{4-}$ have been synthesized and characterized since 1975,[1-3] no arsenic complexes analogous to [(RP)$_2$Mo$_5$O$_{21}$]$^{4-}$ have been reported. After the X-ray crystal structure investigation of the two organophosphonate complexes (NH$_4$)$_4$[(CH$_3$P)$_2$Mo$_5$O$_{21}$]·5H$_2$O and Na[N(CH$_3$)$_4$]-[(NH$_3$C$_2$H$_4$P)$_2$Mo$_5$O$_{21}$]·5H$_2$O, Stalick and Quicksall accounted for the inability to isolate the corresponding As$_2$Mo$_5$ ions. They said that the larger covalent radius of arsenic (1.22 vs 1.10 Å for phosphorus) might sterically inhibit the formation of heteropolyanions of this type with molybdenum.[4] In this paper, it is clearly demonstrated that (RAs)$_2$Mo$_5$ polyanions can be formed in spite of earlier speculations about molecular dimensions.

Experimental Section

As part of a program to explore organic derivatives of heteropoly complexes, we have been able to prepare colorless crystals of both (CN$_3$H$_6$)$_4$[(*n*-C$_3$H$_7$As)$_2$Mo$_5$O$_{21}$]·2H$_2$O and (CN$_3$H$_6$)$_4$[(*n*-C$_3$H$_7$As)$_2$Mo$_6$O$_{24}$] on mixing aqueous solutions of Na$_2$MoO$_4$ and *n*-C$_3$H$_7$AsO(OH)$_2$ (2:1 molar ratio) at pH 4-5 and boiling. These heteropolyanions are highly soluble in water. Tests for cations show that sodium, potassium, cesium, tetramethylammonium, tetraethylammonium, calcium, barium, and magnesium salts are very soluble, but the guanidinium salts can be easily precipitated and separated. After several recrystallizations, we found that two different types of crystals, which can

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