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Photoluminescence Properties of Chloro Amine Complexes of Platinum(IV)

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Introduction

The photochemical and photophysical properties of d^6 metal ion complexes have received considerable mechanistic attention over the past several decades.[2] One goal has been to examine systematically the properties of complex ions of different metal and ligand combinations to establish both the generalities and discontinuities in the excited-state behavior of homologous systems. Among those d^6 complexes commonly accessible, the coordination compounds of platinum(IV) have received relatively modest photochemical[3-5] and photophysical[6] attention. Given some ambiguities in the reported photophysical properties of Pt(IV) systems, the present study was initiated to probe a series of PtA_2Cl_4 complexes, where A = NH_3, $^1/_2$ bpy, or $^1/_2$ phen (bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline). Also described are some data regarding related $PtA_4Cl_2^{2+}$ complexes.

Experimental Section

Syntheses. The platinum(IV) complexes *cis*-$Pt(NH_3)_2Cl_4$ (I),[7] Pt(bpy)Cl_4 (II),[8] Pt(phen)Cl_4 (III),[9] [Pt(en)(bpy)Cl_2]$(ClO_4)_2$ (IV),[10] (en = ethylenediamine), $[Pt(bpy)_2Cl_2][NO_3]_2$ (V),[10] and $[Pt(phen)_2Cl_2]Cl_2$ (VI)[11] were prepared in good yields and recrystallized by published procedures. The phen and bpy complexes were washed with toluene in order to ensure that free ligand impurities did not complicate the emission spectra. Spectroscopic properties (IR and UV/vis) agreed with published values. The proton NMR spectra of IV and V in D_2O solution indicated these to have the trans and cis configurations, respectively.

Photoluminescence Techniques. Luminescence emission and excitation spectra were recorded by using a SPEX Fluorolog 2 Model III emission spectrometer interfaced to a Datamate computer station. Emission spectra were corrected for phototube response, and excitation spectra, for lamp and instrumentation characteristics. Lifetime measurements were carried out by using a system[12] based on a Q-switched Nd/YAG laser operating in the third harmonic (355 nm) as the excitation source. Emission properties were investigated at 77 K (except where noted) and samples were either powdered solids or glassy solutions.

Table I. Photophysical Properties of Various Tetrachloroplatinum(IV) Complexes at 77 K

	$K_2[PtCl_6]^a$	*cis*-$Pt(NH_3)_2Cl_4$	Pt(bpy)Cl_4	Pt(phen)Cl_4
$\bar{\nu}_{max}(em)^b$	1.503	1.695	1.565	1.484
$\Delta\bar{\nu}_{1/2}(em)^c$	0.23	0.249	0.241	0.228
$\bar{\nu}_{max}(ex)^d$		2.294	2.336	2.315
$(\bar{\nu}(em) + \bar{\nu}(ex))/2^e$		1.99	1.95	1.90
$E^{00}(calcd)^f$	1.77^g	2.02	2.00	1.79
τ^i	$\sim 100^h$	17	11	11

[a] Data from ref 6f. [b] Emission maximum in μm^{-1}. [c] Emission bandwidth at half the maximum height. [d] Low-energy excitation maximum in μm^{-1}. [e] Average of $\nu_{max}(em)$ and $\nu_{max}(ex)$. [f] E^{00} in μm^{-1} calculated according to the equation $E^{00} = E_{max}(emission) + 1.29\Delta\nu_{1/2}$, which is drawn from the estimate that E^{00} is the energy at which the intensity of the emission band is 1% of that at the maximum.[17] [g] E^{00} calculated by using the intensity distributions in the vibrational progressions with the theoretical line shape function.[6f] [h] Nonexponential decay at 77 K.[6a] [i] In μs.

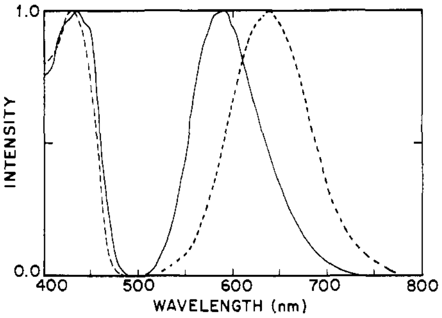

Figure 1. Solid line: emission (λ_{ex} = 350 nm) and long-wavelength excitation (λ_{mon} = 590 nm) spectra of solid *cis*-$Pt(NH_3)_2Cl_4$ at 77 K. Dashed line: emission (λ_{ex} = 320 nm) and long-wavelength excitation (λ_{mon} = 640 nm) spectra of solid Pt(bpy)Cl_4 at 77 K.

Results and Discussion

Key emission properties of several tetrachloroplatinum(IV) complexes are listed in Table I. A major problem encountered during the luminescence studies was the appearance of emissive platinum(II) impurities. The origins of these impurities were severalfold, including Pt(II) starting materials for the syntheses. In general such Pt(II) impurities could be removed by careful recrystallization, although for $[Pt(phen)_2Cl_2]Cl_2$, an extraction method was also used.[13] Another source of Pt(II) impurities results from the relative ease by which Pt(IV) compounds undergo photochemical reduction. Thus, certain photolysis samples would change their emission spectral and lifetime properties during the course of a photophysical investigation, especially if subjected to repetitive pulse laser excitation. The latter problem, while persistent, was generally addressed by minimizing sample irradiation and by repeatedly checking the emission spectral and lifetime properties to determine whether sample degradation had occurred as the result of the measurements.

***cis*-$Pt(NH_3)_2Cl_4$ (I).** In the solid state at 77 K, the emission spectrum of I showed a strong, broad band centered at 1.695 μm^{-1} ($\Delta\nu_{1/2}$ = 0.249 μm^{-1}, $\Delta\bar{\nu}_{1/2}$ defined as full width at half the maximum height) with a weak, apparently vibronic, structure ($\Delta\bar{\nu} \approx 0.06\ \mu m^{-1}$) (Figure 1). Pulsed-laser experiments (λ_{ex} = 355 nm) showed the emission to decay according to a simple exponential function with a lifetime $\tau = 17 \pm 1.5\ \mu s$. The excitation spectrum of solid I at 77 K (λ_{mon} = 590 nm) displayed a lowest energy band with $\bar{\nu}_{max}$ at 2.294 μm^{-1} ($\Delta\bar{\nu}_{1/2} \approx 0.25\ \mu m^{-1}$) and a somewhat more defined vibronic structure ($\Delta\bar{\nu} \approx 0.06\ \mu m^{-1}$) that

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(13) In the case of $[Pt(phen)_2Cl_2]Cl_2$, solutions prepared from seemingly very good quality products continued to show luminescence properties indicating the presence of impurities. Therefore, the orange crystals were first washed with CH_3CN to remove a suspected Pt(phen)Cl_4 impurity, then extracted three times with 10-mL portions of aqueous 0.1 N HCl solution. This left a small residue believed to contain Pt(phen)Cl_4 and Pt(phen)Cl_2 which are insoluble in the aqueous HCL. The volume of the combined HCL extracts was reduced to 5 mL under vacuum, and the resulting yellow solution was filtered and used to prepare samples for luminescence lifetime and spectral measurements.

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nearly mirrors the emission band (Figure 1). The absorption spectrum of this compound in 298 K aqueous solution shows a weak, broad shoulder at ~2.439 μm^{-1} (ϵ = 20 M^{-1} cm^{-1}), which has been assigned[14] as the lowest energy ligand field (LF) singlet to triplet absorption band. On the basis of these observations, the emission band can be assigned to luminescence from a ^{3}LF excited state,[15] the vibronic structure apparently reflecting some coupling to the Pt–N stretching mode.[16] The average of the emission and excitation band maxima energies gives an estimate for E^{00} = 1.99 μm^{-1}. An alternative method of estimating E^{00} based on the assumption of a Gaussian (intensity vs energy) emission band shape[17] gave the comparable value 2.02 μm^{-1}.

Pt(bpy)Cl$_4$ (II). The emission spectrum of II as a powdered solid at 77 K displays a strong, broad band with $\bar{\nu}_{max}$ = 1.565 μm^{-1} (Figure 1). The excitation spectrum was quite analogous to that of the diammine complex described above; i.e., the low-energy excitation band, centered at $\bar{\nu}_{max}$ = 2.336 μm^{-1}, essentially mirrors the emission band. However, the Stokes shift between the excitation and emission maxima is larger than for I. Lifetime measurements showed single-exponential decay with τ = 11 ± 1 μs. In room-temperature acetonitrile solution, II displays a strong, vibronically structured, bipyridine π–π^* absorption band centered at 308 nm. At lower energy are much weaker, poorly resolved shoulders at ~368 and ~420 nm (~2.38 μm^{-1}), possible due to ligand field transitions. In a 77 K MeOH/EtOH (3/1) glassy solution, II showed a broad emission band centered at 1.515 μm^{-1} ($\Delta\bar{\nu}_{1/2}$ = 0.224 μm^{-1}) with a hint of vibronic structure ($\Delta\bar{\nu}$ ~ 0.05 μm^{-1}) and a lifetime τ = 17 ± 2 μs, while the excitation spectrum displayed a broad band with $\bar{\nu}_{max}$ ~ 2.35 μm^{-1}. On the basis of these observations, the emission spectrum of II is also assigned as originating from a ^{3}LF state.[18,19]

Pt(phen)Cl$_4$ (III). In analogy to the photophysical properties of I and II, the emission spectrum of powdered III at 77 K showed a strong, broad band with $\bar{\nu}_{max}$ = 1.484 μm^{-1} and weak vibronic structure ($\Delta\bar{\nu}$ ~ 0.05 μm^{-1}). Lifetime measurements gave exponential decay of the emission with τ = 10.5 ± 1.6 μs. The excitation spectrum showed a low-energy band with $\bar{\nu}_{max}$ = 2.315 μm^{-1} ($\Delta\bar{\nu}_{1/2}$ = 0.22 μm^{-1}) and vibronic structure ($\Delta\bar{\nu} \approx$ 0.06 μm^{-1}). In 3/1 MeOH/EtOH solution the absorption spectrum of III was dominated by the very strong phenanthroline π–π^* absorption band at 270 nm, which has counterparts in the solution spectra of phen complexes of Rh(III) and of Pt(II).[19,20] The emission spectrum of III in 77 K glassy solution (3/1 MeOH/EtOH) shows a single unstructured broad band at $\bar{\nu}_{max}$ = 1.504 μm^{-1} ($\Delta\bar{\nu}_{1/2}$ = 0.22 μm^{-1}), which underwent exponential decay with τ = 24.9 ± 1.5 μs.

[Pt(en)(bpy)Cl$_2$](ClO$_4$)$_4$ (IV), [Pt(bpy)$_2$Cl$_2$](ClO$_4$)$_2$ (V), and [Pt(phen)$_2$Cl$_2$]Cl$_2$ (VI). All three of these complexes presented serious problems with photodecomposition to Pt(II) species. Qualitatively, however, it was observed that the emission spectra of freshly prepared solid samples of the recrystallized IV and V and LiCl solutions of VI[13] were entirely different from those shown in Figure 1. In each case, the spectrum proved to be highly structured, as shown in Figure 2 for IV. Lifetime measurements gave τ values (77 K) in the 10–20-μs range for each compound, but nonexponential decays indicated the presence of a longer lived component of lesser intensity. In addition, even relatively gentle probing of the spectra or lifetimes using either continuous or pulse photolysis led quickly to shifts in the emission spectra (however, retaining the same general patterns, e.g., Figure 2) as well as lifetime changes indicative of Pt(II) formation. (It is notable that the Pt(II) analogue of IV, [Pt(bpy)(en)](ClO$_4$)$_2$, has a π–π^* emission very close to that for IV.)[19] On the basis of these qualitative observations, one can conclude that the emissive state for each of these tetraamine complexes is a ligand-centered π–π^* state, presumably the lowest energy triplet. However, it is not clear whether the nonexponential decays observed (77 K) are the result of competitive deactivations from nonequilibrated states in individual metal complexes, of different microenvironments in the Pt(IV) crystals or, most likely, of the presence of the ubiquitous Pt(II) impurities formed by Pt(IV) photoreduction.

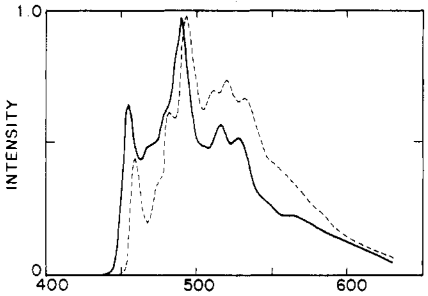

Figure 2. Solid line: emission spectrum (λ_{ex} = 340 nm) of solid [Pt(en)(bpy)Cl$_2$](ClO$_4$)$_2$ at 77 K. Dashed line: emission spectrum (λ_{ex} = 340 nm) of solid [Pt(en)(bpy)](ClO$_4$)$_2$ at 77 K.

Summary

Table I summarizes the photophysical properties of complexes I–III as well as of PtCl$_6^{2-}$. The similarity between the emission spectra of II and III to that of I indicates a common assignment of the emitting state as the lowest energy ^{3}LF state in contrast to an earlier assignment[6b] as a metal to ligand charge-transfer state, ^{3}MLCT, for II and for III. (Furthermore, the estimated E^{00} values of these emissions (~2.0 μm^{-1}) are significantly less than normally found for π–π^* emissions from other 1,10-phenanthroline and 2,2′-bipyridine complexes (~2.2 μm^{-1}).[20]) If one views the three d^6 *cis*-diamines as having an approximately D_{4h} symmetry with the two amines in the *xy* plane and trans chlorides on the *z* axis, the lowest energy excited state would be the ^{3}E, i.e. having the $(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1$ one-electron configuration. Thus, it would not be surprising that this LF state would be relatively insensitive to the nature of the amines, although the energy order (based upon λ_{max} or either of the estimates of E^{00}) places I as having a ligand field stronger than that of either II or III. This is opposite to the normal observation that the bidentate aromatic amines are stronger field than NH$_3$;[21] however, this minor reversal can no doubt be attributed to the relatively poor π-back-bonding expected from a metal ion in an oxidation state as high as Pt(IV).

For the tetraamine Pt(IV) systems, the presence of a nitrogen donor ligand at four (rather than two) of the coordination sites in either the cis (V and VI) or trans (IV) configuration apparently raises the lowest ^{3}LF excited state above the lowest $^3\pi$–π^* states of bpy (IV and V) or phen (VI). If one assumes that the highest energy feature of each π–π^* emission spectrum represents the ligand-centered 0–0 transition, the E^{00} values for these $^3\pi$–π^* states can be estimated as 2.22, 2.24, and 2.24 μm^{-1} for IV–VI, respectively. The ^{3}LF state E^{00} energy of the *trans*-Pt(NH$_3$)$_4$Cl$_2^{2+}$

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(15) (a) This assignment faces some ambiguity given that frozen solutions of *cis*-Pt(NH$_3$)$_2$Cl$_2$, a possible impurity, display a weak emission at the same frequency; however, this luminescence is too weak to be measurable in solid KBr pellets, unlike the strong emission observed for the solid samples of *cis*-Pt(NH$_3$)$_2$Cl$_4$ described here.[15b] (b) Patterson, H. H.; Tewksbury, J. C.; Martin, M.; Krogh-Jespenson, M. B.; LoMenzo, J. A.; Hoper, H. O.; Vismanath, A. K. *Inorg. Chem.* **1981**, *20*, 2297.

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ion has been estimated to be 2.22 μm^{-1}, and that of *trans*-Pt$(en)_2Cl_2^{2+}$, to be 2.25 μm^{-1} from previous luminescence experiments.[6g] Thus the reversal in the relative orders of the ^{3}LF and $^3\pi-\pi^*$ energies in the tetraamine complexes results from the higher ligand field strength.[22,23] The apparent proximity of the ^{3}LF and $^3\pi-\pi^*$ energies might be expected to lead to dual emissions from some of these species as has been reported for certain Rh(III) and Ir(III) analogues;[23] however, multiple emissions of this type could not be differentiated from those resulting from the apparent photoproduction of Pt(II) impurities.

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Registry No. *cis*-$Pt(NH_3)_2Cl_4$, 16893-05-3; $Pt(bpy)Cl_4$, 16949-85-2; $Pt(phen)Cl_4$, 17030-27-2.

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(22) For analogous Rh(III) complexes, the tetrachloro complex Rh(phen)Cl_4^- displays a ^{3}LF emission with E^{00} about 1.6 μm^{-1}, the dichloro complexes *cis*-$Rh(phen)_2Cl_2^+$ and $Rh(bpy)_2Cl_2^+$ display ^{3}LF emissions with E^{00}'s about 1.9 μm^{-1}, while the tris(diimine) complexes Rh$(phen)_3^{3+}$ and $Rh(bpy)_3^{3+}$ display ligand-centered $^3\pi-\pi^*$ emissions with E^{00}'s about 2.22 μm^{-1}.[20,23,24]

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Reactions of $ReH_7(PPh_3)_2$ with 1-(Diphenylphosphino)-2-(diphenylarsino)ethane (arphos) and 1,2-Bis(diphenylarsino)ethane (dpae). Structural Characterization of $ReH_5(PPh_3)_2$(arphos-*As*) and $ReH_5(PPh_3)_2$(dpae-*As*)

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Introduction

The thermal reactions of the polyhydride complex $ReH_7(PPh_3)_2$ with monodentate σ donors (L) to form complexes of stoichiometry $ReH_5(PPh_3)_2L$ are well documented.[2-4] We have recently investigated the reactions of this complex with the bidentate donors 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos) and 1,2-bis(diphenylarsino)ethane (dpae) with the object of probing the donor ability of the P and As atoms of the former ligand. Following the completion of our work, a publication appeared[5] that described the results of related studies on the reactions of several $ReH_7(PR_3)_2$ complexes (PR_3 = P-*i*-Pr_3, PPh_3, $P(C_6H_{11})_3$) with a range of bidentate phosphines. While the complexes isolated by Shaw and co-workers[5] differ from those that are the subject of the present report, several bear a close resemblance, in particular $ReH_5(PPh_3)_2$(dppm-*P*) and $ReH_5[P(C_6H_{11})_3]_2$(dppe-*P*), which contain monodentate $Ph_2PCH_2PPh_2$ and $Ph_2PCH_2CH_2PPh_2$, respectively. In the present report we describe the isolation and characterization of the linkage isomers $ReH_5(PPh_3)_2$(arphos-*P*) and $ReH_5(PPh_3)_2$(arphos-*As*) and of the analogous complex $ReH_5(PPh_3)_2$(dpae-*As*). Details of their NMR spectra and electrochemical properties are presented along with crystallographic data for the isostructural pair $ReH_5(PPh_3)_2$(arphos-*As*) and $ReH_5(PPh_3)_2$(dpae-*As*).

Table I. Crystallographic Data for $ReH_5(PPh_3)_2$(arphos-*As*)$\cdot 0.5C_6H_6$ (**2**) and $ReH_5(PPh_3)_2$(dpae-*As*)$\cdot 0.5C_6H_6$ (**3**)

	2	**3**
chem formula	$ReAsP_3C_{65}H_{62}$	$ReAs_2P_2C_{65}H_{62}$
fw	1197.26	1241.21
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	9.9934 (9)	10.003 (1)
b, Å	10.5311 (8)	10.571 (1)
c, Å	26.580 (3)	26.625 (3)
α, deg	99.965 (8)	99.86 (1)
β, deg	92.428 (9)	93.037 (9)
γ, deg	92.115 (7)	92.511 (9)
V, Å^3	2749.9 (9)	2766 (1)
Z	2	2
T, °C	20	20
λ(Mo Kα), Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.446	1.490
μ(Mo Kα), cm^{-1}	29.59	35.06
transm coeff	1.00–0.85	1.00–0.87
R^a	0.036	0.020
$R_w{}^b$	0.046	0.027

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Experimental Section

Starting Materials. The complex $ReH_7(PPh_3)_2$ was prepared according to reported methods.[6] The ligand 1,2-bis(diphenylarisono)ethane (dpae) was purchased from Aldrich Chemical Co., while 1-(diphenylphosphino)-2-(diphenylarsino)ethane (arphos) was obtained from Strem Chemicals Inc. Both were used without further purification. All solvents were obtained from commercial sources and were deoxygenated with dinitrogen gas prior to use.

Reaction Procedures. All reactions were performed under an atmosphere of dry dinitrogen gas with the use of standard Schlenk techniques.

A. Syntheses of $ReH_5(PPh_3)_2$(arphos-*P*) (1) and $ReH_5(PPh_3)_2$(arphos-*As*) (2). This complex was obtained as an approximately 50:50 mixture of its P- and As-bound isomers. A mixture of $ReH_7(PPh_3)_2$ (0.102 g, 0.142 mmol) and arphos (0.124 g, 0.281 mmol) was refluxed in 15 mL of ethanol for 2 h. The white precipitate was filtered off, washed with ethanol (2 × 15 mL) and methanol (3 × 15 mL), and dried under vacuum; yield 0.134 g (79%). Microanalytical data were in accord with the presence of a small amount of water of crystallization. Anal. Calcd for $C_{62}H_{61}AsOP_3Re$ (i.e. $ReH_5(PPh_3)_2(arphos)\cdot H_2O$): C, 63.30; H, 5.23. Found: C, 62.28; H, 5.07. IR spectroscopy (Nujol mull) showed ν(OH) at ca. 3350 (m, br) and δ(OH) at ca. 1650 (w) cm^{-1}.

B. Synthesis of $ReH_5(PPh_3)_2$(dpae-*As*) (3). A mixture of $ReH_7(PPh_3)_2$ (0.180 g, 0.251 mmol) and dpae (0.240 g, 0.493 mmol) was refluxed in 15 mL of toluene for 2 h. The yellow solution was cooled to 0 °C, and 50 mL of pentane was added to induce precipitation of a white solid. The solid was filtered off, washed with pentane (2 × 15 mL), and dried under vacuum; yield 0.140 g (45%). Anal. Calcd for $C_{62}H_{61}As_2OP_2Re$ (i.e. $ReH_5(PPh_3)_2(dpae)\cdot H_2O$): C, 61.03; H, 5.04. Found: C, 60.14; H, 5.03. IR spectroscopy supported the presence of a small amount of water of crystallization.

When this same reaction was carried out in refluxing ethanol (same procedure as described in section A), a similar product was obtained. Anal. Found: C, 61.46; H, 5.24. However, NMR spectroscopy (in C_6D_6) showed that two products were present, one of which was **3**, and that these had very similar properties. These two products showed Re–*H* resonances as binomial triplets at δ −4.83 and −5.13, the latter being due to **3**. The $^{31}P\{^1H\}$ spectrum of this mixture was characterized by singlets at δ +37.7 and +36.8 (due to **3**).

Preparation of Single Crystals for Structure Determinations. Suitable crystals of $ReH_5(PPh_3)_2$(arphos) were obtained by the slow diffusion of pentane into a benzene solution of the mixture of P- and As-bound isomers (**1** and **2**). The best formed crystals proved to be those of **2**. A similar procedure was used to grow crystals of $ReH_5(PPh_3)_2$(dpae-*As*) (**3**) from a sample of this complex that had been prepared in ethanol.

X-ray Analysis. The structures of $ReH_5(PPh_3)_2$(arphos-*As*)$\cdot 0.5C_6H_6$ (**2**) and $ReH_5(PPh_3)_2$(dpae-*As*)$\cdot 0.5C_6H_6$ (**3**) were determined by the application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table I. The cell constants were

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