lighter. The THF was removed in vacuo and freshly distilled toluene (15 mL added). The solution was then filtered over Celite and concentrated, and hexanes were added to afford a white precipitate (463 mg, 90%), which was filtered and washed with hexanes. ^{1}H NMR (90 MHz, 298 K, CD_2Cl_2): δ 7.81 (d, 3 H), 7.71 (d, 3 H), 6.26 (t, 3 H), 2.07 (s, 8 H). ^{1}H NMR (250 MHz, CD_2Cl_2, 218 K): 7.81 (d, 3 H), 7.71 (d, 3 H), 6.26 (t, 3 H), 2.37 (d, 4 H), 1.61 (d, 4 H) (coalescence ca. 263 K). ^{13}C NMR (250 MHz, CD_2Cl_2, 298 K): δ 139.68, 135.59, 105.85, 29.48. IR (CHCl$_3$): 2478 cm^{-1} (ν_{B-H}). Anal. Calcd for $C_{13}H_{17}BIrN_3$: C, 33.84; H, 3.90; N, 18.21. Found: C, 33.86; H, 3.98; N, 17.35.

(Hydrotris(1-pyrazolyl)borato)dicarbonyliridium(I) (3). Carbon monoxide (1 atm, 20 mL/min) was passed into a THF (10 mL) solution of **2** (78 mg) for 5 min. The THF was removed in vacuo to give a bright yellow solid in quantitative yield identified as **3** by comparison to the spectral properties previously reported.[2] ^{1}H NMR (250 MHz, toluene-d_8): δ 7.45 (d, 3 H), 7.29 (d, 3 H), 5.79 (t, 3 H). IR (Nujol mull): 2485 cm^{-1} (ν_{B-H}); 2084, 2055, 1999, 1978 cm^{-1} (ν_{CO}). IR (heptane): 2074, 2049, 2009, 1974 cm^{-1} (ν_{CO}).

(Hydrotris(1-pyrazolyl)borato)(ethylene)hydro(η^1-vinyl)iridium(III) (4). An ether or acetone solution of **2** (25 mg) in a Pyrex Schlenk tube or borosilicate NMR tube was photolyzed for 2 h at 350 nm. The major product (ca. 90%) was the title vinyl hydride, which was identified by its spectral properties but could not be further purified. ^{1}H NMR (250 MHz, acetone-d_6): δ 7.95–7.4 (m, 6 H), 6.75 (dd, 1 H), 6.34 (t, 1 H), 6.28 (t, 1 H), 6.25 (t, 1 H, J_{app} = 2 Hz), 5.33 (dd, J_{cis} = 10.5 Hz, 1 H, J_{gem} = 3.2 Hz, 1 H), 4.50 (dd, 1 H, J_{trans} = 17.8 Hz), 3.24 (c, 2 H), 2.84 (c, 2 H), −16.57 (s, 1 H); observable resonances of minor product δ 7.8–7.0 (m, 6 H), 6.4–6.3 (m, 3 H), 3.5 (c, 2 H), 3.0 (c, 2 H), −17.16 (s, 1 H).

(Hydrotris(1-pyrazolyl)borato)(ethylene)(methyl acrylate)iridium(I) (5). A dry Schlenk tube was charged with **2** (103 mg, 0.22 mmol), methyl acrylate (43 μL, 0.48 mmol), and THF (10 mL), and this mixture was allowed to stir at 20 °C for 3 h. THF was removed in vacuo. The residue was recrystallized from ether and hexanes to give **5** (95%). ^{1}H NMR (250 MHz, CDCl$_3$, 298 K): δ 7.73 (d, 3 H), 7.66 (d, 3 H), 6.23 (t, 3 H), 3.62 (s, 3 H), 3.13 (b, 1 H), 2.19 (b), 2.26 (c, 1 H), 2.21 (dd, 1 H). ^{1}H NMR (223 K): δ 7.73 (d, 3 H), 7.66 (d, 3 H), 6.23 (t, 3 H), 3.82 (t, 1 H), 3.64 (s, 3 H), 3.06 (dd, 1 H), 2.86 (t, 1 H), 2.74 (t, 1 H), 2.6–2.4 (c, 2 H), 2.11 (t, 1 H). ^{13}C NMR (250 MHz, CDCl$_3$, 298 K):

δ 177.4, 138.9, 135.2, 105.5, 50.6, 49.8, 49.7, 14.0, 13.8. IR (CHCl$_3$): 2483 (ν_{B-H}), 1696 cm^{-1} ν_{CO}. Anal. Calcd for $C_{15}H_{20}BN_6O_2Ir$: C, 34.69; H, 3.88; N, 16.17. Found: C, 33.24; H, 3.85; N, 15.46.

Attempted Alkane C–H Activation. (a) Reaction of 1 with Alkanes above the Decomposition Temperature of 1. A resealable glass pressure vessel charged with **1** (22.5 mg, 0.043 mmol), 3,3-dimethyl-1-butene (0.4 mL, 4.1 mmol), and cyclooctane (1.5 mL) was degassed and filled with argon. The tube was then heated in an oil bath at 150 °C for 12 days, keeping the liquid in the vessel below the surface of the oil and the base of the vessel above the floor of the oil bath. The volatiles were then separated from the organometallic fraction by vacuum transfer. Analysis by the method of Burk and Crabtree[19] showed that only 0.02 mmol of cyclooctene was present.

(b) Reaction of 1 with Alkane below the Decomposition Temperature of 1. A resealable glass pressure vessel charged with **1** (24 mg, 0.047 mmol) and methylcyclohexane (2 mL) was degassed, filled with argon, and heated at (50 °C for 20 h). No olefin was formed, and the ^{1}H NMR spectrum showed **1** was largely unchanged.

(c) Reaction of 1 with Benzene. A resealable glass pressure vessel charged with **1** (21 mg, 0.04 mmol), triphenylphosphine (10 mg, 0.04 mmol), and benzene (1.5 mL) was degassed, filled with argon, and heated (60 °C for 20 h). The ^{1}H NMR spectrum showed only **1** and triphenylphosphine.

(d) Reaction of 1 with Hydrogen. Neither bubbling hydrogen at 1 atm through a solution of **1** nor heating **1** to 42 °C in 1 atm of hydrogen in a resealable glass pressure vessel affords any reaction.

(e) Reaction of 2 with Alkane. A resealable glass pressure vessel charged with **2** (9 mg, 0.02 mmol) and cyclooctane (1.5 mL) was degassed, filled with argon, and heated (70 °C for 18 h). No cyclooctene was formed, and the ^{1}H NMR spectrum showed decomposition products.

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Contribution from the Institute of Chemistry and Technology of Radioelements, CNR, Corso Stati Uniti 4, 35100 Padova, Italy, Institute of Pharmaceutical Chemistry, University of Milano, Viale Abruzzi 42, 20100 Milano, Italy, and Department of Chemistry, Virginia Commonwealth University, Box 2006, Richmond, Virginia 23284

Six-Nitrogen Macrocyclic Complexes of the Dioxouranium(VI) and Praseodymium(III) Ions

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The Schiff-base condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene in the presence of uranyl salts produced complexes of the general formula $[UO_2(C_{30}H_{26}N_6)]X_2$, with X = ClO_4^-, NO_3^-, and CH_3COO^-. A related complex, $[Pr(NO_3)_2(CH_3O-H)(C_{30}H_{26}N_6)](ClO_4)\cdot0.5CH_3OH\cdot0.5H_2O$, was obtained from a similar metal-templated reaction followed by partial anion metathesis. The Pr(III) complex crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$ in a cell having $a = 20.198$ (3) Å, $b = 14.208$ (2) Å, $c = 12.727$ (2) Å, and $\beta = 104.25$ (4)°. In this complex the Pr(III) ion was 11-coordinated, being linked to the six nitrogen atoms of an 18-membered macrocyclic ligand, to two bidentate nitrates situated on opposite sides of the macrocycle, and to one molecule of methanol. A noncoordinated ClO_4^- ion balanced the cationic charge of the complex cation; clathrated water and methanol were also present. The macrocyclic cations existing in these uranyl and praseodymium(III) complexes retained their identity in solution and were moderately inert to metal release in the presence of acids or bases.

Introduction

The condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene was first studied by Stotz and Stoufer,[1] who reported the formation of a yellow crystalline product, $C_{30}H_{26}N_6$, formulated as an 18-membered macrocyclic ligand with a six-nitrogen donor

cavity, L_1 (Figure 1). These authors also reported a dark brown copper(II) product, $[Cu_2(C_{30}H_{26}N_6)](NO_3)_4$, which they considered to be a dinuclear complex of the same ligand, involving Cu–Cu interactions. Reinvestigation of these species by Nelson et al.[2] showed the yellow compound $C_{30}H_{26}N_6$ to have the tricyclic

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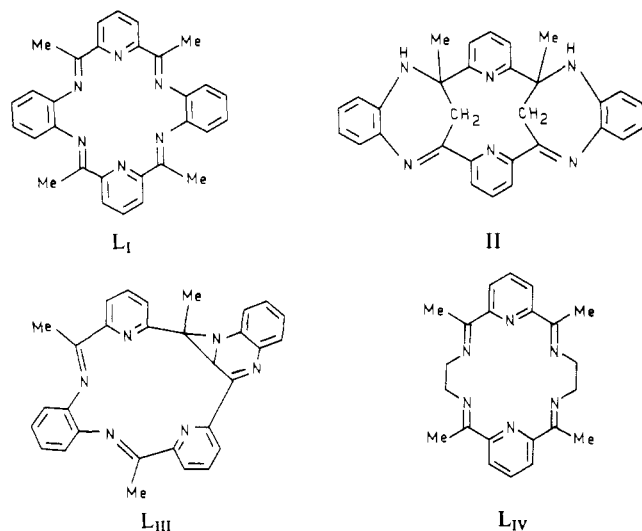(1) Stotz, R. W.; Stoufer, R. C. *J. Chem. Soc., Chem. Commun.* **1970**, 1682.
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Figure 1. Schematic formulas of six-nitrogen macrocycles and related compounds. L_I, L_{III}, and L_{IV} indicate macrocyclic ligands that form identifiable metal complexes; II indicates the tricyclic $C_{30}H_{26}N_6$ molecule, which is not a ligand.

structure II (Figure 1), consisting of a central 12-membered ring flanked by two identical seven-membered rings. Also, the formula of the copper(II) complex was established[3] to be $[Cu(C_{30}H_{26}N_6)(H_2O)](ClO_4)_2 \cdot H_2O$; in this complex, the organic moiety had rearranged to give ligand L_{III}, with an asymmetric four-nitrogen cavity encapsulating a single Cu(II) ion (Figure 1). The existence of metal complexes of the L_I macrocycle was brought back into question by Radecka-Paryzek,[4] who reported derivatives of this ligand with the nitrates of the larger lanthanide ions, La(III) to Nd(III). However, the characterization of these complexes, based on elemental analyses, mass spectra, and partial infrared absorption data, still left doubt about their true structure.

Our interest in this problem originated from our previous studies of the complexes formed by the lanthanide(III)[5,6] and uranyl[7] ions with the 18-membered macrocyclic ligand L_{IV} (Figure 1). The lanthanide complexes of this ligand were remarkable for their exceptional inertness toward metal release in solution—a feature that contrasted with the common behavior of these very labile ions and made possible a detailed study of the luminescence of the europium(III) complex in dilute aqueous solution.[8] The uranyl complexes, which represented the first examples of the UO_2^{2+} ion bound to a six-nitrogen macrocyclic cavity, also had unusual electronic spectra.[9] Complexes of the lanthanide(III) and uranyl ions with the L_I macrocycle, if indeed they could be obtained, would be expected to exhibit similarly interesting properties, especially because the presence of the *o*-phenylene side chains might provide an enhanced electron delocalization within the macrocyclic system.

In consideration of the conflicting literature reports concerning the metal complexes of the $C_{30}H_{26}N_6$ species, we felt that a definitive structural assignment for any such complex should rest on at least one example of crystallographic analysis. Therefore, we diligently searched for, and finally obtained, a complex of this ligand suitable for single-crystal X-ray analysis. We also rein-

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vestigated the experimental conditions leading to the cyclic or noncyclic condensation of the bifunctional precursors of systems L_I and II. We report here both the synthetic and the structural aspects of our investigation.

Experimental Section

Starting Materials and Procedures. 2,6-Diacetylpyridine and 1,2-diaminobenzene were obtained from Aldrich Chemical Co.; the diamine was sublimed under vacuum prior to use. The solvents (Aldrich reagent or spectra grade) were used without further purification. Infrared (IR) spectra and thermogravimetric analyses (TGA) were obtained as described.[5] Nuclear magnetic resonance (NMR) spectra were measured with a JEOL FX 90Q Fourier transform spectrometer, at 89.56 MHz for ^{1}H and 22.50 MHz for ^{13}C. Dimethyl sulfoxide-d_6 and chloroform-d (Aldrich) were used as solvents. Microanalyses were carried out by Atlantic Microlab, Atlanta, GA.

Macrocyclic Complex of Uranyl Perchlorate, $[UO_2(C_{30}H_{26}N_6)](ClO_4)_2$. 2,6-Diacetylpyridine (326 mg, 2.00 mmol) and $UO_2(ClO_4)_2 \cdot 6H_2O$ (577 mg, 1.00 mmol) were dissolved in 30 mL of warm anhydrous methanol and treated with 1,2-diaminobenzene (216 mg, 2.00 mmol in 20 mL of methanol) in a nitrogen-flushed apparatus. The mixture was refluxed for 5 h; during this time the color changed gradually from yellow to dark greenish brown and an olive-colored solid formed. The solid was filtered off, washed with methanol, and dried in vacuo; its IR and NMR spectra showed the presence of the tricyclic compound $C_{30}H_{26}H_6$ (II),[2] together with a uranyl perchlorate complex. The solid mixture was repeatedly extracted with boiling tetrachloroethylene to remove the purely organic component; the undissolved dark green uranyl complex was rinsed with methanol and dried in vacuo at room temperature; yield ca. 40%. Anal. Calcd for $UO_2(C_{30}H_{26}N_6)(ClO_4)_2$: C, 38.37; H, 2.79; N, 8.14. Found: C, 38.48; H, 2.83; N, 8.91. IR absorptions (cm^{-1}) and selected assignments: 3095 w; 3025 vvw; 2980 vvw, 2940 vw; 1615 m, ν(C=N); 1595 s, ν(C=N); 1490 m; 1450 m; 1375 s; 1340 vw; 1270 s; 1195 vw; 1155 vw; 1100–1085 vs, br, ν_3 of ionic ClO_4^-; 1015 vw; 1011 m; 990 sh; 945 s, $\nu_3(UO_2^{2+})$; 830 sh; 820 m–s; 800 vw; 770 m; 765 m; 750 m; 745 m; 725 w; 620 s, ν_4 of ionic ClO_4^-; 570 w; 530 w; 500 vw; 440 vw.

The complex was soluble in dimethyl sulfoxide and dimethylformamide to give greenish solutions; it was insoluble in other common organic solvents and water. Relevant NMR spectral data are reported in the Results and Discussion.

Macrocycle Formation in the Presence of Uranyl Nitrate or Acetate. The reaction was carried out as described for the corresponding perchlorate and produced the nitrate and acetate salts, respectively, of the $[UO(C_{30}H_{26}N_6)]^{2+}$ cation. However, these salts were always obtained as mixtures with compound II, from which they could not be completely separated owing to their similar solubilities. The complexes were identified by their IR and NMR spectra; yields were estimated to be less than 20%.

Macrocyclic Tris(nitrato)lanthanide Complexes, $[M(NO_3)_3$-$(C_{30}H_{26}N_6)] \cdot nH_2O$ (M = La(III), Pr(III), Nd(III); $n = 0.5$–3.0). Repeated attempts to obtain these complexes by exactly following the procedure described in ref 4 consistently failed. In each case, the first and major product was the tricyclic II (yield, 40–60%), together with a heterogeneous mixture of solid substances from which no complex could be isolated either by chromatography or by fractional crystallization. However, minute yields of the desired complexes were obtained by the following modified procedure: The reactants (2,6-diacetylpyridine, lanthanide nitrate hexahydrate, 1,2-diaminobenzene) were refluxed in methanol for 4 h as described for the uranyl perchlorate complex. The solid formed (silky light yellow needles of II; yields 40–60%) was quickly removed from the hot solution by gravity filtration on a pleated paper filter. The clear bright yellow solution was allowed to stand, covered and undisturbed, at 0 °C for 1 day. After this time, a new crop of II (fluffy needles) had formed in the solution, while a small amount of tiny yellow crystals (prisms) had formed on the walls and bottom of the flask. The solution with the suspended II was removed, and the yellow crystals adhering to the flask were washed with a small volume of methanol, collected, and dried over P_4O_{10}. If the crystals, upon IR examination, appeared to contain II as an impurity, this was removed by repeated washing with hot chloroform. Yields of the pure lanthanide complexes ranged between 1 and 5% relative to the starting materials. Anal. Calcd for $La(NO_3)_3(C_{30}H_{26}N_6) \cdot 0.5H_2O$: C, 44.51; H, 3.73; N, 15.07. Found: C, 44.50; H, 3.70; N, 15.08. Calcd for $Pr(NO_3)_3(C_{30}H_{26}N_6) \cdot 2H_2O$: C, 43.21; H, 3.63; N, 15.12. Found: C, 43.23; H, 3.63; N, 15.16. Calcd for $Nd(NO_3)_3(C_{30}H_{26}N_6) \cdot 3H_2O$: C, 42.15; H, 3.77; N, 14.75. Found: C, 42.02; H, 3.81; N, 14.71.

The three complexes had virtually superimposable IR spectra; a listing of IR absorption (cm^{-1}) with selected assignments is given here for the La(III) complex: 3630 s, ν_{asym}(OH$_2$); 3550 s, ν_{sym}(OH$_2$); 3115 sh; 3100 m; 3030 vw; 2985 vw; 2940 vw; 1635 s, ν(C=N); 1595 s, ν(C=N); 1490

sh, 1455 vs, vbr, ν(N=O) of bidentate chelating NO_3^-; 1425 sh; 1375 m; 1325 vs, br, $\nu(NO_2)$ of bidentate chelating NO_3^-; 1305 sh; 1255 s; 1235 m; 1195 w; 1160 vw; 1145 vw; 1115 w; 1035 m; 995 m; 980 w; 955 vw; 815 w; 804 vs; 795 w; 765 s; 740 m–s; 725 m–s; 705 sh; 650 vw; 555 sh; 545 m; 525 vw; 505 vw; 495 vw; 410 vs, vbr, $\rho(OH_2)$.

The complexes were slightly soluble in hot methanol and dimethyl sulfoxide. The ^1H NMR spectrum of the La(III) complex in DMSO-d_6 gave broad, poorly resolved signals that changed with time. Chemical shifts of freshly prepared solutions (δ, ppm, relative to TMS): complex pattern (8.60; 8.51, 7.98, 7.45, 7.1), 14 H, py and bz; (2.80, 1.85) 12 H, CH_3.

The yellow mother liquor remaining after separation of the macrocyclic complex was concentrated to a small volume under reduced pressure, diluted with 1:1 diethyl ether–hexane, and chilled in a refrigerator for 1 day. A first crop of yellow crystals (yields 10–20%) was identified as the 1:1 condensation product $C_{15}H_{15}N_3O \cdot nH_2O$ (V), discussed later. A second crop appeared to be a mixture of V with salts of its brick red protonated derivative; in some instances the white metal nitrate (starting material) was also present. The components of the mixture could be detected and partly separated (by hand) under a microscope and identified by their distinctive IR spectra.

$[Pr(NO_3)_2(CH_3OH)(C_{30}H_{26}N_6)](ClO_4) \cdot 0.5CH_3OH \cdot 0.5H_2O$. The tris(nitrato) complex $[Pr(NO_3)_3(C_{30}H_{26}N_6)] \cdot 2H_2O$ (20 mg, 2.4 × 10⁻² mmol) was dissolved in hot methanol (5 mL) and treated with an excess of $LiClO_4$ (10 mg, 9.4 × 10⁻² mmol in 2 mL of methanol). The mixture was loosely stoppered and kept undisturbed at 40 °C for several hours. The yellow crystals that formed were decanted, washed with 1 mL of chilled methanol, and dried at 60 °C; yield ca. 80%.

$Nd(C_{30}H_{26}N_6)(OH)(NO_3)_{0.5}(ClO_4)_{1.5} \cdot 2H_2O$. The tris(nitrato) complex $[Nd(NO_3)_3(C_{30}H_{26}N_6)] \cdot 3H_2O$ (50 mg, 5.8 × 10⁻² mmol) was dissolved in warm methanol (3 mL) containing NaOH (2 mg, 5 × 10⁻² mmol) to aid dissolution. An excess of lithium perchlorate (20 mg, 2.0 × 10⁻¹ mmol in 4 mL of methanol) was added, and the solution was kept undisturbed at 40 °C for several hours. Small yellow crystals formed and were decanted, washed with chilled methanol, and dried at 60 °C; yield ca. 80%. Anal. Calcd for $Nd(C_{30}H_{26}N_6)(OH)(NO_3)_{0.5}(ClO_4)_{1.5} \cdot H_2O$: C, 42.83; H, 3.72; N, 10.84. Found: C, 42.67; H, 3.60; N, 10.78. IR absorptions (cm⁻¹) and selected assignments: 3600 sh; 3540–3350 m, vbr, ν(OH); 3120 sh; 3110 m; 3020 sh; 2980 vw; 2940 w; 1630 s, ν(C=N); 1595 vs, ν(C=N); 1480 vs, ν(N=O) of bidentate chelating NO_3^-; 1380 s; 1310 s, $\nu(NO_2)$ of bidentate chelating NO_3^-; 1250 s; 1195 m; 1160 vw; 1130 w; 1115 vw; 1085 vs, ν_3 of ionic ClO_4^-; 1035 w; 1000 m; 985 m; 975 w; 900 m; 825 w; 815 m; 805 m; 785 w; 765 m; 740 m; 710 sh; 705 sh; 630 w; 605 m, ν_4 of ionic ClO_4^-; 555 w; 505 w; 495 vw.

Nontemplated Condensation Products and Their Hydrochlorides. The 2:2 condensation product $C_{30}H_{26}N_6$ (II) was prepared as described by Nelson et al.[2] When this compound (100 mg, 2.13 × 10⁻¹ mmol) was dissolved in hot chloroform (150 mL) and an excess of HCl gas was passed through the solution, the color changed from yellow to deep red and a dark red crystalline solid separated almost immediately. The product was filtered, washed with chloroform, and dried in vacuo at room temperature. The yield was quantitative. Anal. Calcd for $C_{30}H_{26}N_6 \cdot$ $2HCl \cdot H_2O$: C, 64.17; H, 5.39. Found: C, 64.12; H, 5.41.

A solution of 2,6-diacetylpyridine (816 mg, 5.00 mmol) and 1,2-diaminobenzene (540 mg, 5.00 mmol) in 40 mL of ethanol was refluxed for 4 h in a nitrogen-flushed apparatus, and the resulting yellow solution was evaporated to dryness under reduced pressure. The yellow-orange residue was dissolved in a small volume (3 mL) of warm methanol, and the resulting suspension was filtered to remove any undissolved material. The clear solution was diluted with 1:2 diethyl ether–hexane until cloudy and chilled for several hours in a freezer. A fluffy precipitate (silky hairlike yellow needles) formed and was filtered off and dried at 60 °C. The water content in the final product depended upon the extent of drying; yields approximately 40%. The crystalline product V (mp 156 °C) was very soluble in most organic solvents, including diethyl ether; it was insoluble in hexane and water. The solutions were unstable and darkened when exposed to air, depositing a brown gum after a few hours. Anal. Calcd for $C_{15}H_{15}N_3O \cdot 0.25H_2O$: C, 70.02; H, 6.06; N, 16.30. Found: C, 70.16; H, 5.29; N, 16.72. IR absorptions (cm⁻¹) and selected assignments: 3380 m, $\nu(NH_2)$; 3080 vv; 2995 m; 2950 m–w; 2890 w; 1710 vs, sharp ν(C=O); 1625 s; 1610 sh; 1595 vs; 1500 sh; 1480 vs; 1460 vs; 1430 m; 1365 s; 1350 s; 1310 m; 1250 m–s; 1240 sh; 1220 sh; 1175 sh; 1160 w; 1130 w; 1110 w; 1080 vw; 1040 vw; 1015 vvw; 993 w; 960 vw; 930 vw; 880 vw; 810 m; 740 vs; 720 sh; 645 vw; 590 vw; 550 vw; 470 vw; 400 vw.

The ^1H NMR spectrum of a freshly prepared (yellow) solution of V in deuterochloroform consisted of two sets of broad and ill-resolved resonances at δ (ppm, relative to TMS internal standard) 8.3–6.8 (7 H) and 2.7–1.3 (ca. 6 H). The broadness of these signals suggested the existence of both syn- and anti-imine forms. No reliable ^{13}C NMR data

were obtained, as the solution darkened during the time required to record the spectrum.

Gaseous HCl was passed through a solution of V (50 mg) in dichloromethane (30 mL) at 0 °C. The color changed to bright red, and a brick red crystalline solid separated almost immediately. The solid was filtered, washed with diethyl ether, and dried in vacuo at room temperature. The yield was quantitative. Anal. Calcd for $C_{15}H_{15}N_3O \cdot HCl \cdot$ $1.5H_2O$: C, 56.87; H, 6.05; N, 13.27. Found: C, 56.90; H, 5.55; N, 13.52.

X-ray Measurements and Structure Determination. The crystal and refinement data for $[Pr(NO_3)_2(CH_3OH)(C_{30}H_{26}N_6)](ClO_4) \cdot 0.5CH_3O$-$H \cdot 0.5H_2O$ (pale yellow transparent prisms) are summarized in Table I. A prismatic single crystal of dimensions 0.24 × 0.16 × 0.36 mm was lodged in a Lindemann glass capillary and centered on a four-circle Philips PW 1100 diffractometer with graphite-monochromated Mo Kα radiation. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random and varying each of the orientation angles χ and φ over a range of 120°, with 5 ≤ θ ≤ 8°. For the determination of precise lattice parameters, 25 strong reflections with 10 ≤ θ ≤ 14° were considered. Integrated intensities for hkl reflections with $l > 0$ were measured, and two standard reflections, $-7,0,3$ and $0,-4,5$, were monitored every 180 min. There were no significant fluctuations of intensities other than those expected from Poisson statistics.

The intensity data were corrected for Lorentz–polarization effects and for absorption, by following the method of North et al.;[10] no correction was made for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined with a blocked matrix (two blocks) because of the large number of variables, with anisotropic thermal parameters assigned to all the non-hydrogen atoms, except the carbon atoms C(7), C(15), C(30), C(22) and C(9), C(10), C(11), C(12) and C(24), C(25), C(26), C(27), which were refined isotropically in order to reduce the number of variables.

Hydrogen atoms were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement (d_{C-H} = 0.95 Å and U_{iso} = 0.07 Å²). The function minimized was $\sum w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. The anomalous dispersion terms[11] for Pr were taken into account in the refinement. Atomic scattering factors were taken from ref 11. Data processing and computation were carried out by using the SHELX 76 program package.[12]

The refinement of the $[Pr(NO_3)_2(CH_3OH)(C_{30}H_{26}N_6)](ClO_4) \cdot 0.5C$-$H_3OH \cdot 0.5H_2O$ complex reached convergency at $R = 0.061$. At this point two residuals about 2 e/Å³ were evident in the Fourier difference map. They were interpreted as a statistically distributed half-molecule of methanol per $[Pr(NO_3)_2(CH_3OH)(C_{30}H_{26}N_6)]ClO_4$ unit. Another minor residual (1 e/Å³) could be interpreted as a half-molecule of water.

The introduction of the methanol and water molecules in the positions indicated by the electron density residuals with a population factor of 0.5 gave the most significant lowering of the R values: $R = 0.036$ and R_w = 0.035.

Results and Discussion

Lanthanide Macrocycles. In our experiments, the condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene in the presence of the nitrate of lanthanum(III), praseodymium(III), or neodymium(III), when carried out under the conditions described by Radecka-Paryzek,[4] yielded chiefly the metal-free tricyclic compound II and the metal-free "half-cycle" $C_{15}H_{15}N_3O \cdot nH_2O$ (V; discussed later), rather than the metal macrocycles reported by that author. However, minute yields of metal-containing com-

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Table II. Atomic Coordinates ($\times 10^4$) for Non-Hydrogen Atoms and U_{eq} Values ($\times 10^3$) with Esd's in Parentheses

	x/a	y/b	z/c	U_{eq},[a] Å^2	PP[b]
Pr	3876.0 (1)	7009.3 (2)	2519.0 (2)	26.8 (1)	
N(1)	4947 (19)	7890 (3)	3750 (3)	35 (2)	
N(2)	4990 (2)	7288 (3)	1767 (3)	34 (1)	
N(3)	3754 (2)	7072 (3)	391 (3)	31 (1)	
N(4)	2710 (2)	7586 (3)	1204 (3)	31 (1)	
N(5)	2741 (2)	7032 (3)	3230 (3)	33 (1)	
N(6)	3972 (2)	7201 (3)	4628 (3)	36 (2)	
C(1)	4928 (2)	8169 (4)	4763 (4)	39 (2)	
C(2)	5406 (3)	8810 (4)	5342 (5)	52 (2)	
C(3)	5892 (3)	9163 (5)	4864 (5)	60 (3)	
C(4)	5921 (3)	8870 (4)	3864 (5)	55 (2)	
C(5)	5439 (2)	8230 (4)	3315 (4)	41 (2)	
C(6)	5456 (2)	7878 (4)	2208 (4)	40 (2)	
C(7)	6002 (3)	8246 (5)	1716 (5)	62 (2)*	
C(8)	4975 (2)	6829 (4)	771 (4)	35 (2)	
C(9)	5544 (3)	6428 (4)	518 (4)	44 (1)*	
C(10)	5470 (3)	5945 (4)	−4378 (5)	52 (2)*	
C(11)	4847 (3)	5829 (4)	−1147 (5)	52 (2)*	
C(12)	4276 (3)	6211 (4)	−896 (4)	43 (1)*	
C(13)	4330 (2)	6716 (4)	56 (4)	33 (2)	
C(14)	3285 (3)	7536 (4)	−248 (4)	34 (2)	
C(15)	3302 (3)	7865 (5)	−1351 (5)	60 (2)*	
C(16)	2681 (2)	7802 (3)	171 (4)	36 (2)	
C(17)	2110 (3)	8228 (4)	−505 (5)	46 (2)	
C(18)	1564 (3)	8448 (4)	−88 (5)	52 (2)	
C(19)	1584 (3)	8213 (4)	966 (5)	44 (2)	
C(20)	2168 (2)	7783 (3)	1607 (4)	34 (2)	
C(21)	2209 (2)	7490 (4)	2735 (4)	36 (2)	
C(22)	1629 (3)	7767 (4)	3237 (5)	56 (2)*	
C(23)	2814 (3)	6628 (4)	4271 (4)	36 (2)	
C(24)	2306 (3)	6090 (4)	4551 (4)	46 (1)*	
C(25)	2440 (3)	5633 (4)	5556 (5)	53 (2)*	
C(26)	3078 (3)	5697 (4)	6259 (5)	54 (2)*	
C(27)	3585 (3)	6218 (4)	5975 (5)	48 (1)*	
C(28)	3462 (3)	6700 (4)	4994 (4)	38 (2)	
C(29)	4386 (3)	7766 (4)	5225 (4)	38 (2)	
C(30)	4355 (3)	8080 (4)	6336 (5)	56 (2)*	
O(1)	4008 (2)	8750 (3)	1734 (3)	48 (2)	
O(2)	3569 (2)	8730 (3)	3108 (3)	48 (2)	
O(3)	3218 (2)	5582 (2)	1497 (3)	41 (1)	
C(33)	2644 (3)	5129 (4)	1819 (5)	50 (2)	
O(4)	3954 (2)	5391 (2)	3639 (3)	43 (1)	
O(5)	4797 (2)	5737 (3)	2976 (4)	54 (2)	
O(6)	4760 (2)	4378 (3)	3738 (4)	173 (2)	
O(7)	3853 (2)	10067 (3)	2503 (3)	64 (2)	
N(11)	3809 (2)	9202 (3)	2446 (4)	43 (2)	
N(22)	4514 (2)	5144 (3)	3479 (4)	36 (2)	
Cl(1)	2544 (1)	−499 (1)	6276 (1)	50 (1)	
O(11)	2281 (3)	365 (4)	5767 (4)	102 (3)	
O(21)	3136 (3)	−306 (4)	7093 (4)	102 (3)	
O(31)	2086 (2)	−918 (5)	6800 (5)	114 (3)	
O(41)	2711 (4)	−1078 (5)	5527 (5)	159 (4)	
O$_{Me}$	5104 (12)	751 (17)	974 (19)	216 (10)*	0.5
C$_{Me}$	4552 (12)	27 (17)	393 (19)	138 (8)*	0.5
O$_W$	4671 (11)	945 (15)	1156 (17)	189 (8)*	0.5

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor. Starred values indicate that the atoms were refined isotropically. [b] Population parameters (PP) are reported when $\neq 1$.

pounds, having the general formula $[M(NO_3)_3(C_{30}H_{26}N_6)]\cdot m H_2O$ (M = La(III), Pr(III), Nd(III); m = 0.5–3.0) could be obtained by the procedure described in the Experimental Section. The formulation of these compounds as tris(nitrato) complexes of the macrocyclic ligand L_I containing variable amounts of lattice water, was based on their analytical composition and IR absorption spectra, which showed the following distinctive features (cm⁻¹): (a) 3630 (vs, sharp, $\nu_{asym}(OH_2)$) and 3550 (s, sharp, $\nu_{sym}(OH_2)$) for non-hydrogen-bonded, noncoordinated water; (b) 1455 (vs) and 1330 (vs), both broad, ν_5 and ν_1 of bidentate chelating NO_3^-; (c) 1630 (vs), 1595 (vs), both sharp, $\nu(C=N)$ of Schiff base and pyridine; (d) a large number of very sharp and well-resolved absorptions, the pattern of which was different from that of compound II and practically identical with the pattern of the

Table III. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses

(a) Praseodymium Environment			
Pr–N(1)	2.651 (4)	Pr–O(1)	2.705 (4)
Pr–N(2)	2.681 (4)	Pr–O(2)	2.675 (4)
Pr–N(3)	2.660 (4)	Pr–O(3)	2.592 (3)
Pr–N(4)	2.661 (4)	Pr–O(4)	2.690 (4)
Pr–N(5)	2.664 (4)	Pr–O(5)	2.557 (4)
Pr–N(6)	2.657 (4)		
N(1)–Pr–N(2)	60.5 (1)	N(4)–Pr–N(5)	60.5 (1)
N(1)–Pr–N(6)	60.6 (1)	N(5)–Pr–N(6)	60.7 (1)
N(2)–Pr–N(3)	60.5 (1)	O(1)–Pr–O(2)	47.0 (1)
N(3)–Pr–N(4)	60.2 (1)	O(4)–Pr–O(5)	48.0 (1)

(b) Ligands			
N–C(py)	1.346 (7)	C–C(phen)	1.388 (8)
Cl–O	1.399 (6)	C–C(aliphatic)	1.499 (9)
N(11)–O(1)	1.254 (7)	N(22)–O(4)	1.247 (6)
N(11)–O(2)	1.263 (7)	N(22)–O(5)	1.275 (6)
N(11)–O(7)	1.233 (6)	N(22)–O(6)	1.209 (6)
C(33)–O(3)	1.470 (7)		
Pr–N(1)–C(5)	120.4 (3)	N(4)–C(16)–C(14)	116.8 (4)
Pr–N(1)C(1)	119.2 (3)	C(14)–C(16)–C(17)	120.8 (5)
C(1)–N(1)–C(5)	118.9 (4)	N(4)–C(16)–C(17)	122.3 (5)
Pr–N(2)–C(8)	114.6 (3)	C(15)–C(14)–C(16)	117.9 (5)
Pr–N(2)–C(6)	122.1 (4)	N(3)–C(14)–C(15)	125.4 (5)
C(6)–N(2)–C(8)	122.8 (5)	N(3)–C(14)–C(16)	116.6 (4)
Pr–N(3)–C(14)	122.5 (3)	C(16)–C(17)–C(18)	118.8 (5)
Pr–N(3)–C(13)	114.5 (3)	C(17)–C(18)–C(19)	119.2 (5)
C(13)–N(3)–C(14)	121.8 (4)	C(18)–C(19)–C(20)	119.7 (5)
Pr–N(4)–C(20)	120.0 (3)	N(4)–C(20)–C(19)	121.0 (5)
Pr–N(4)–C(16)	120.4 (3)	C(19)–C(20)–C(21)	121.9 (5)
C(16)–N(4)–C(20)	118.9 (4)	N(4)–C(20)–C(21)	117.0 (4)
Pr–N(5)–C(23)	114.4 (3)	N(5)–C(21)–C(20)	117.5 (5)
Pr–N(5)–C(21)	121.8 (4)	C(20)–C(21)–C(22)	118.1 (5)
C(21)–N(5)–C(23)	123.2 (5)	N(5)–C(21)–C(22)	124.4 (5)
Pr–N(6)–C(29)	122.9 (4)	N(5)–C(23)–C(28)	116.6 (5)
Pr–N(6)–C(28)	113.6 (3)	N(5)–C(23)–C(24)	123.2 (5)
C(28)–N(6)–C(29)	123.0 (4)	N(6)–C(28)–C(27)	123.8 (5)
N(1)–C(1)–C(29)	117.5 (4)	N(6)–C(28)–C(23)	117.1 (5)
N(1)–C(1)–C(2)	120.8 (5)	N(6)–C(29)–C(1)	116.8 (5)
C(2)–C(1)–C(29)	121.7 (5)	C(1)–C(29)–C(30)	117.8 (5)
C(1)–C(2)–C(3)	118.8 (6)	N(6)–C(29)–C(30)	125.4 (5)
C(2)–C(3)–C(4)	120.4 (6)	Pr–O(1)–N(11)	97.1 (3)
C(3)–C(4)–C(5)	119.2 (6)	Pr–O(2)–N(11)	98.3 (3)
N(1)–C(5)–C(4)	121.8 (5)	Pr–O(3)–C(33)	123.0 (3)
C(4)–C(5)–C(6)	121.0 (5)	Pr–O(4)–N(22)	95.2 (3)
N(1)–C(5)–C(6)	117.2 (5)	Pr–O(5)–N(22)	101.0 (3)
N(2)–C(6)–C(5)	116.4 (5)	O(2)–N(11)–O(7)	121.5 (5)
C(5)–C(6)–C(7)	117.8 (5)	O(1)–N(11)–O(7)	121.4 (5)
N(2)–C(6)–C(7)	125.9 (5)	O(1)–N(11)–O(2)	117.0 (4)
N(2)–C(8)–C(13)	116.4 (5)	O(5)–N(22)–O(6)	121.8 (5)
N(2)–C(8)–C(9)	124.0 (5)	O(4)–N(22)–O(6)	122.5 (5)
N(3)–C(13)–C(12)	123.2 (5)	O(4)–N(22)–O(5)	115.6 (4)
N(3)–C(13)–C(8)	117.4 (4)	O–Cl–O	109.4 (4)
C–C–C(phen, av)	120.0 (6)		

macrocyclic praseodymium nitrate perchlorate complex, discussed below.

The tris(nitrato) complexes were obtained as very small yellow crystals, unsuitable for X-ray analysis; systematic attempts to improve crystal quality by partial substitutions of the nitrates with other counterions finally produced two new crystalline complexes, $[Pr(C_{30}H_{26}N_6)(NO_3)_2(CH_3OH)](ClO_4)\cdot0.5CH_3OH\cdot0.5H_2O$ and $Nd(C_{30}H_{26}N_6)(OH)(NO_3)_{0.5}(ClO_4)_{1.5}\cdot2H_2O$, having ligand IR absorption patterns identical with each other and with those of the parent tris(nitrato) complexes. The praseodymium(III) bis(nitrato) perchlorate complex was obtained as well-formed crystals, and X-ray analysis revealed the presence of the highly symmetrical six-nitrogen macrocyclic entity described in the following section.

X-ray Analysis of the Pr(III) Complex. Fractional coordinates for the non-hydrogen atoms of the complex are listed in Table II; bond parameters are listed in Table III and torsion angles of the macrocycle in Table IV. The structure of the $[Pr(NO_3)_2$-$(CH_3OH)(C_{30}H_{26}N_6)]^+$ complex cation is shown in Figure 2. An

Table IV. Torsion Angles

| atoms 1-4	2-3 dist, Å	1-2-3-4 angle, deg
C(1)-N(1)-C(5)-C(6)	1.341 (7)	178.0 (5)
N(1)-C(5)-C(6)-N(2)	1.504 (8)	1.0 (7)
C(5)-C(6)-N(2)-C(8)	1.281 (6)	174.2 (5)
C(6)-N(2)-C(8)-C(13)	1.420 (7)	−140.7 (5)
N(2)-C(8)-C(13)-N(3)	1.402 (6)	0.1 (7)
C(8)-C(13)-N(3)-C(14)	1.427 (7)	−135.8 (5)
C(13)-N(3)-C(14)-C(16)	1.271 (6)	175.2 (4)
N(3)-C(14)-C(16)-N(4)	1.495 (8)	4.5 (7)
C(14)-C(16)-N(4)-C(20)	1.337 (7)	177.8 (4)
C(16)-N(4)-C(20)-C(21)	1.348 (7)	177.1 (4)
N(4)-C(20)-C(21)-N(5)	1.478 (8)	−3.2 (7)
C(20)-C(21)-N(5)-C(23)	1.280 (6)	173.3 (5)
C(21)-N(5)-C(23)-C(28)	1.418 (7)	−140.0 (5)
N(5)-C(23)-C(28)-N(6)	1.407 (7)	2.5 (7)
C(23)-C(28)-N(6)-C(29)	1.421 (7)	−138.7 (6)
C(28)-N(6)-C(29)-C(1)	1.268 (6)	174.5 (5)
N(6)-C(29)-C(1)-N(1)	1.479 (8)	1.3 (7)
C(29)-C(1)-N(1)-C(5)	1.359 (7)	178.9 (5)
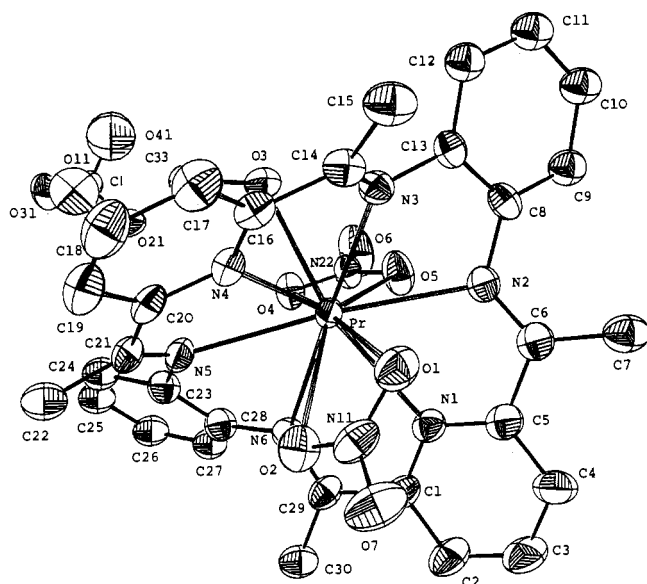
Figure 2. Perspective view of the macrocyclic complex [Pr(NO₃)₂(C-H₃OH)(C₃₀H₂₆N₆)](ClO₄). The thermal ellipsoids are at 50% probability.

ordered perchlorate ion balances the positive charge of the complex cation; clathrated methanol and water (a half-molecule of each per unit of complex) are also present.

The praseodymium(III) ion is 11-coordinate, being linked to the six nitrogen atoms of the macrocyclic ligand L_I, to a bidentate chelating nitrate and to a methanol molecule on one side of the macrocycle, and to another bidentate chelating nitrate on the other side. The macrocycle itself is folded, with the two pyridine rings directed away from the hemisphere containing the NO₃⁻ and CH₃OH ligands. Similar structures, in which two coordinated nitrates occupy opposite sides of a folded macrocycle and a coordinated solvent molecule is present on the convex side, have been observed[13] for the cerium(III) complex of the six-nitrogen macrocycle L_{IV} [Ce(NO₃)₂(H₂O)(L_{IV})]⁺ and for the gadolinium(III) complex[14] of the 18-crown-6 ligand [GdCl₂(C₂H₅OH)(18-crown-6)]⁺.

The conformation of the macrocyclic ligand L_I, shown for clarity without the metal ion in Figure 3, is fairly symmetrical and is characterized by a dihedral angle of 110.3 (1)° between the planes of the two pyridine rings (N(3)-C(14)···C(21)-N(5)) and by a dihedral angle of 112.0 (2)° between the planes of the two o-phenylene rings. This extensive bending prevents conjugation

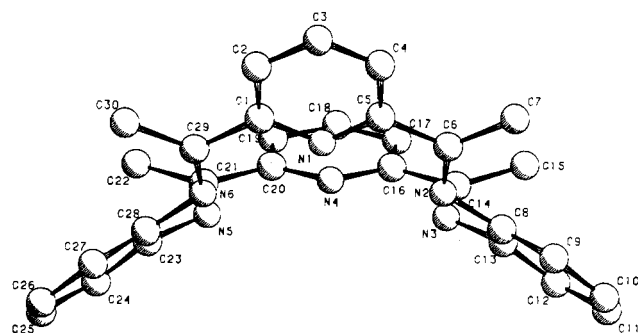(13) Arif, A. M.; Backer-Dirks, J. D. J.; Gray, C. J.; Hart, F. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1987**, 1665.
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Figure 3. Conformation of the $C_{30}H_{26}N_6$ ligand in the Pr(III) complex.

Table V. Metal–Nitrogen Bond Lengths and Dihedral Angles in Six-Nitrogen Lanthanide Macrocycles

complex[a]	coord no.	av M–N bond length, Å pyridine	av M–N bond length, Å imine	dihedral angle, deg
[LaL_{IV}(NO₃)₃]	12[b]	2.755	2.708	153.3
[CeL_{IV}(NO₃)₂(H₂O)]⁺	11[b]	2.682	2.673	121.0
[NdL_{IV}(NO₃)(H₂O)₂]²⁺	10[b]	2.621	2.610	116.1
[LuL_{IV}(CH₃COO)(H₂O)]²⁺	9[c]	2.556	2.541	114.0
[PrL_I(NO₃)₂(CH₃OH)]⁺	11[d]	2.658	2.663	113.0 (py–py) 112.1 (bz–bz)

[a] $L_{IV} = C_{22}H_{26}N_6$; $L_I = C_{30}H_{26}N_6$. [b] Reference 13. [c] Reference 6. [d] This work.

among the four aromatic sections of the macrocycle. The torsion angles C(29)-N(6)-C(28)-C(23) = 139.5 (9)°, C(6)-N(2)-C-(8)-C(13) = −140.9 (8)°, C(28)-C(23)-N(5)-C(21) = 139.0 (9)°, and C(8)-C(13)-N(3)-C(14) = −135.4 (9)° indicate that the two o-phenylene groups joined to the imine moieties considerably reduce the flexibility of the cycle compared to that of ligand L_{IV}, in which the =N—CH₂—CH₂—N= side chains function as adjustable hinges. In the Pr^{III}–L_I complex, bending occurs chiefly at the bonds adjacent to the o-phenylene groups, namely N(6)-C(28) and C(23)-N(5) on one side of the macrocycle and N(2)-C(8) and C(13)-N(3) on the other side.

The roughly planar halves of the macrocycle that include the pyridine rings are not identical, in that the half-cycle closer to the coordinated methanol (donor atom O(3)) departs from planarity more than the other half-cycle. (Deviations from the best mean plane range from −0.068 (4) to 0.045 (6) Å for the N-(2)-C(6)···C(29)-N(6) plane and from −0.022 (5) to 0.016 (4) Å for the N(3)-C(14)···C(21)-N(5) plane.) The presence of the coordinated methanol also slightly affects the symmetry of the NO₃⁻ ligands: The two Pr–O bond lengths for the NO₃⁻ group adjacent to the CH₃OH ligand (Pr-O(4) = 2.690 (4) Å and Pr-O(5) = 2.557 (4) Å) differ from each other more than do those of the "lone" NO₃⁻ group (Pr-O(1) = 2.705 (4) Å and Pr-O(2) = 2.675 (4) Å). This lengthening of the Pr-O(4) bond relative to the Pr-O(5) bond may occur in order to increase the distance between the nitrate oxygen and the nearest nonbonded atoms. (In this respect significant intramolecular contacts are O(4)···O-(3)_{methanol} = 2.778 (5) Å and O(4)···C(28) = 2.874 (7) Å.) If the average Pr–O_{nitrate} bond lengths are considered, however, the less symmetric NO₃⁻ group adjacent to the CH₃OH (average Pr–O_{nitrate} = 2.623 Å) is actually slightly closer to the metal than the lone NO₃⁻ group wedged between the two pyridine rings (average Pr–O_{nitrate} = 2.690 Å). Longer metal–oxygen distances for the lone nitrate have also been observed[13] in [Ce(NO₃)₂(H₂O)(L_{IV})]⁺ (2.71 Å for lone NO₃⁻ vs 2.68 Å for NO₃⁻ adjacent to coordinated H₂O).

It is instructive to compare the crystallographic features of the Pr(III) complex described in this work with those of several six-nitrogen macrocycles of the lanthanides that have recently become available.[6,13] The metal–nitrogen bond lengths and dihedral angles for a series of structurally related complexes of ligands L_{IV} and L_I are collected in Table V; it may be observed that the M–N bond lengths decrease fairly regularly as the metal

ionic radii decrease along the lanthanide series. In the Pr(III) complex of L_I, however, the difference between the M–$N_{pyridine}$ and the M–N_{imine} bond lengths virtually disappears, and all M–N bonds become equal within the limits of their standard deviations. Thus, the greater rigidity of the o-phenylene macrocycle results in an increased regularity in the metal–nitrogen bond lengths.

The dihedral angle between the halves of the macrocycle containing the pyridine rings also decreases with decreasing metal ionic radius, but the variation is far from regular. For ligand L_I, the change in angle is 32° from La(III) to Ce(III), (Δ ionic radius 0.03 Å)),[15] 5° from Ce(III) to Nd(III) (Δ ionic radius 0.04 Å), and 2° from Nd(III) to Lu(III) (Δ ionic radius 0.15 Å). For ligand L_I in the Pr(III) complex (the only complex of this ligand so far investigated by X-ray analysis), the pyridine–pyridine dihedral angle is 11° smaller than that of the Ce^{III}–L_{IV} complex, even though the difference in the metal ionic radii is less than 0.02 Å. It may be concluded that the folding of the macrocycle is the result of various cooperative factors, among which the rigidity of the ligand, the size of the metal ion, and the number and bulk of the exocyclic ligands appear to be the most important.

Uranyl Macrocycles. The Schiff-base condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene, in the presence of the stoichiometric quantity of uranyl perchlorate, produced a mixture of a uranyl complex and of the tricyclic compound II. Repeated extraction of the solid product with boiling tetrachloroethylene succeeded in completely removing the organic component. The insoluble fraction, an olive green powder insoluble or only sparingly soluble in most solvents, had an elemental analysis corresponding to $UO_2(C_{30}H_{26}H_6)(ClO_4)_2$. Its IR spectrum showed the following features: (a) the UO_2^{2+} antisymmetric stretching absorption at 940 cm⁻¹ (strong, very sharp); (b) the ν_3 and ν_4 modes of ionic ClO_4^- at 1090 cm⁻¹ (very strong, broad) and 620 cm⁻¹ (medium), respectively; (c) the absence of absorption arising from –OH, >NH, or >C=O functionalities; (d) the "macrocyclic ligand" pattern, identical with that of the praseodymium(III) dinitrate perchlorate complex discussed in the preceding section.

The carbon-13 and proton NMR spectra of the uranyl perchlorate complex in dimethyl sulfoxide-d_6 solution gave the following results, which did not change with time and were consistent with the presence of the highly symmetrical ligand L_I: ¹³C chemical shifts (δ, ppm, relative to TMS internal standard) 180.0 (C=N), 155.4 (α-C of py), 141.3 (γ-C of py), 129.6 (β-C of py), 178.7 (C-1 of bz), 130.6, 123.8 (C-2 and C-3 of bz), 21.13 (CH₃); ¹H chemical shifts (δ, ppm, relative to TMS internal standard) 9.16–8.80 (complex pattern, 6 H, py), 7.95–7.61 (complex pattern, 8 H, benzene), 3.37 (singlet, 12 H, CH₃). These values agreed with those reported for the macrocyclic complexes of the uranyl ion with ligand L_{IV}.[7] Also, the pattern of the three H atoms of the 2,6-disubstituted pyridine rings was identical with that observed for the lutetium(III) macrocyclic complex of ligand L_{IV},[6] indicating a similar bonding arrangement. Similar results were obtained when the condensation reactions were carried out in the presence of uranyl nitrate or acetate. However, the uranyl–L_I nitrate and acetate complexes, although clearly identified by their infrared spectra, could not be completely separated from the byproduct II.

Condensation in the Absence of Metal Salts. As a reference for the metal-templated reactions, we carried out the condensation of the organic precursors under similar conditions but without metal salts. In one set of experiments, a small quantity of a strong acid (ca. 10⁻⁵ M H_2SO_4) was added to mimic the "acidity" resulting from the hydrolysis of metal salts. The major product of

the acid-catalyzed reaction was II; smaller quantities of another product, $C_{15}H_{15}N_3O \cdot nH_2O$ (V) with n = 0.25–0.75, were also obtained. Compound V (yellow needles, very soluble in most organic solvents) was the major condensation product in the absence of an acid catalyst; it was identified as the 1:1 Schiff base of the bifunctional precursors. Its infrared spectrum showed a medium, broad band at 3320 cm⁻¹, arising from the stretching vibration of the –NH₂ group, and a sharp, strong absorption at 1700 cm⁻¹, due to the C=O stretching mode.

In the presence of acids, compounds II and V were immediately protonated to give intensely colored salts, e.g., $C_{30}H_{26}N_6 \cdot 2H$-Cl·2H₂O (deep red, nearly black small crystals) and $C_{15}H_{15}N_3O \cdot HCl \cdot nH_2O$ (red prisms). The infrared spectra indicated that protonation had occurred at the >NH groups of II and at the –NH₂ group of V, as expected from the higher basicity of secondary and primary amino groups compared to pyridine and imine nitrogens. In solution, the protonated species were stable only in the presence of an excess of acid. When the crystalline salts were dissolved in nonacidic solvents, partial deprotonation occurred; addition of a base completely restored the original unprotonated species. Indeed these compounds, because of the marked color difference of their basic and acid forms, behaved like pH indicators.

In view of the established rearrangement of II to the four-nitrogen-donor ligand L_{III} by reaction with Cu(II) salts,[3] it appeared worthwhile to explore whether II might rearrange to L_I by interaction with large metal ions known to favor coordination to six-nitrogen-donor macrocycles. We therefore attempted to react II with salts of Ag⁺, Hg²⁺, Cd²⁺, Pb²⁺, Sr²⁺, Ba²⁺, and several lanthanides. The solid products obtained, of varied non-stoichiometric compositions, appeared to be "adducts" in which the organic component had retained the original structure II. Some of these adducts had colors and infrared spectra that suggested the presence of the partly protonated II, resulting from hydrolysis of the metal salts.

Conclusions

Our investigation has achieved two main objectives of general usefulness. First, we have clarified the previously confused situation regarding the products of the metal-templated Schiff-base condensation of 2,6-diacetylpyridine and 1,2-diaminobenzene. We have established that, in the presence of metal ions of suitable size and coordination ability, the condensation can be indeed directed to yield metal complexes of the symmetrical six-nitrogen-donor macrocyclic ligand L_I. Under the conditions of our experiments, the yields of metal macrocycles were always minor compared to those of the purely organic condensation products—the tricyclic $C_{30}H_{30}N_6$ (II) and the "half-cycle" $C_{15}H_5N_3 \cdot nH_2O$ (V). Once formed, however, the complexes were thermally very stable; they were also moderately inert toward release of the metal ion in solution, even in the presence of added acids or bases. Second, we have provided X-ray structural data that, when used in conjunction with the more easily accessible yet distinctive IR and/or NMR data, will permit the reliable rapid identification of any new metal complex presumed to contain the L_I macrocycle.

(15) Shannon, R. D. *Acta Crystallogr.*, *Sect. A* **1976**, *32*, 751.