lower in energy, in agreement with experiment, than singlet and triplet tetrahedral minima by 176 and 6.3 kcal mol^{-1}, respectively.

In our previous study[23] of η^2-tetraperoxides, $M(O_2)_4^{2-}$, small distortions of each MO_2 fragment from a symmetrical, isosceles triangle geometry were observed, i.e. one M–O bond shorter than the other. INDO/1 calculations were able to reproduce this experimentally observed distortion for $Nb(O_2)_4^{3-}$ and $Mo(O_2)_4^{2-}$.[23]

The five-coordinate complex NbF_5 was optimized within the constraints of D_{3h} (trigonal-pyramidal) and C_{4v} (square-pyramidal) symmetry. These minima are calculated to be within $^1/_2$ kcal mol^{-1} of each other. The specific geometry at each minimum is of interest. For the TBP5 and SQP5 geometries the $Nb{-}F_{ax}$ and $Nb{-}F_{basal}$ bonds, respectively, are calculated to be longer than the $Nb{-}F_{eq}$ and $Nb{-}F_{apical}$ bonds, respectively, in keeping with basic electronic structural arguments.[24]

For seven-coordinate structures NbF_7^{2-} and ZrF_7^{3-}, the different polytopes were compared in two distinct ways. First, the M–F bonds were kept fixed ("frozen") and idealized (in terms of bond angles) seven-coordinate structures assumed. Second, these idealized, frozen structures were allowed to relax, for NbF_7^{2-}, by submitting them to a geometry optimization. Three seven-coordinate polytopes[25] were considered: the pentagonal bipyramid (PBP7), capped octahedron (CO7), and capped trigonal prism (CTP7). These structures are calculated to be close in energy, as expected. For the frozen approximation the PBP7 is favored on the basis of smaller nuclear–nuclear repulsions. For the fully optimized NbF_7^{2-} structures the CO7 was calculated to be the global minimum by 3 kcal mol^{-1} versus the PBP7. The CTP7 relaxes to the PBP7. In the PBP7, NbF_7^{2-}, the $Nb{-}F_{ax}$ bonds are shorter than the $Nb{-}F_{eq}$ bonds, in keeping with previous analyses.[25]

In the geometry optimization of $Rh(NH_3)_5Cl^{2+}$, an interesting result is obtained: $R(\mathrm{RH{-}Cl}) = 243$ pm, $R(\mathrm{Rh{-}N}) = 214$ pm, and $R(\mathrm{Rh{-}N_{trans}}) = 217$ pm. Thus, the INDO/1 geometry optimization correctly describes the well-known "trans" influence;[23] i.e., the bond trans to Cl^- is longer than those which are cis.

Although this work does not represent an exhaustive study of the INDO/1 model for the calculation of geometric quantities for second-row transition-metal species, the results allow several conclusions to be drawn. First, INDO/1 does as good a job in predicting geometries as does minimal basis set ab initio calculations on large, coordinatively saturated molecules. Second, the INDO/1 method in the majority of the cases studied here reproduces the energy ordering of geometric isomers.

It should be emphasized again that no exhaustive or comprehensive investigation has been made of the INDO/1 parameters. That the model works as well as it does with so little effort testifies to the strength of the model. We believe that very useful results can be obtained by this model, but as always, the proper care of interpretation must be exercised.

Acknowledgment. This work was supported in part by a grant from the U.S. Army through a CRDEC (Aberdeen, MD) Center of Excellence Award to the University of Florida. Additional funding by the National Science Foundation is gratefully acknowledged.

---

(22) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980; p 65.

(23) Cundari, T. R.; Zerner, M. C.; Drago, R. S. *Inorg. Chem.* **1988**, *27*, 4239.

(24) Whangbo, M.-H.; Burdett, J. K.; Albright, T. *Orbital Interactions in Chemistry*; Wiley: New York, 1970.

(25) Hoffmann, R.; Beier, B. F.; Muetterties, E. L.; Rossi, A. R. *Inorg. Chem.* **1977**, *6*, 55.

(26) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, PA, **1977**; p 704.

(27) Present address: Department of Chemistry, Bloomsburg University, Bloomsburg, PA 17815.

Department of Chemistry and Quantum
Theory Project
University of Florida
Gainesville, Florida 32611

Wayne P. Anderson[27]
Thomas R. Cundari
Russell S. Drago*
Michael C. Zerner*

Received June 30, 1989

Isolation and Characterization of $IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2$: A Neutral Dihydrogen Complex of Iridium

The nature of metal–hydrogen interactions in iridium polyhydride complexes has been the focus of several recent studies.[1–4] All reported iridium nonclassical, η^2-dihydrogen[2,3] complexes have been cationic while the neutral iridium polyhydride complexes that have been studied appear to be classical hydrides.[1,5] In contrast, we have isolated $IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2$ (**1**) in which dihydrogen is coordinated to a neutral iridium center. The metal–hydrogen interactions in **1** exhibit dynamic behavior that we have examined both in solution and in the solid state. This dynamic behavior is remarkably different than that which has been observed[2,3] for cationic η^2-hydrogen iridium complexes.

We initially obtained **1** through treatment of THF solutions of $IrCl_3{\cdot}3H_2O$ and 2 equiv of $P(i\text{-}Pr)_3$ with 2 equiv of sodium naphthalide under an atmosphere of hydrogen (Scheme I). Filtration of the reaction mixture, followed by removal of the THF solvent, produced an oil from which orange crystals of **1** arose upon standing under an atmosphere of H_2. The crystals were found to contain an equimolar amount of napthalene. The polyhydride complex **1** is stable only in the solid state under an atmosphere of hydrogen and slowly converts to $IrH_2Cl[P(i\text{-}Pr)_3]_2$[6] (**2**), through elimination of H_2 under 1 atm of argon. In solution, **1** was found to establish an equilibrium with **2** through the reversible loss of H_2 (Scheme I).[7] Prompted by these observations, we have discovered that **1** can be prepared more conveniently through the reaction of **2** with H_2 either in solution or the solid state. Thus, a pentane solution of **2** placed under 1 atm of hydrogen and allowed to stand at room temperature gives rise to orange crystals[8] of the less soluble **1** in 70–80% yield.

Scheme I

$$IrCl_3{\cdot}3H_2O + 2P(i\text{-}Pr)_3 + 2NaC_{10}H_8 \xrightarrow[\text{THF/25 °C}]{H_2}$$
$$IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2 \rightleftharpoons IrH_2Cl[P(i\text{-}Pr)_3]_2 + H_2$$

The ^{1}H NMR spectrum of a sample of **1** in CD_2Cl_2 solution at 22 °C under 1 atm of hydrogen exhibits a broad ($\omega_{1/2} \approx 700$ Hz) singlet at ca. −17 ppm. Reduction of the hydrogen pressure by partial evacuation results in the resonance sharpening and moving up field toward a limiting value of −33.0 ppm, the chemical shift which is observed for the hydride resonance of **2** under an atmosphere of argon at 22 °C. A sample of **1** that was dissolved in CD_2Cl_2, freeze/pump/thaw degassed and allowed to stand under an atmosphere of argon for 12 h was seen to produce a hydride signal identical with that observed for **2** (δ −33.0 ppm, $J_{P-H} = 13$ Hz). Conversely, spectra identical with those of **1** under

---

(1) Garlaschelli, L.; Khan, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212–7213.

(2) Crabtree, R. H.; Lavin, M.; Bonneviot, L. *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037.

(3) (a) Rhodes, L. F.; Caulton, K. G. *J. Am. Chem. Soc.* **1985**, *107*, 259–260. (b) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165–1167.

(4) (a) Heinekey, D. M.; Payne, N. G.; Schulte, G. K. *J. Am. Chem. Soc.* **1988**, *110*, 2303–2305. (b) Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. *J. Am. Chem. Soc.* **1989**, *111*, 3088–3089.

(5) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.

(6) Werner, H.; Wolf, J.; Hohn, A. *J. Organomet. Chem.* **1985**, *287*, 395–407.

(7) A similar equilibrium has been suggested (Mura, P.; Segre, A.; Sostero, S. *Inorg. Chem.* **1989**, *28*, 2853–2858) as part of the solution behavior of $Ir^{IV}H_2Cl_2[P(i\text{-}Pr)_3]_2$. However, the solution behavior of **1** (see below) does not suggest further equilibria with paramagnetic Ir(IV) species.

(8) ^{1}H NMR (300 MHz, 20 °C in CD_2Cl_2 under 1 atm H_2): δ 2.36 (m, 6 H), 1.26 (m, 36 H), −17.0 (br s). $^{31}P\{^1H\}$ NMR (122 MHz, 20 °C in CD_2Cl_2 under 1 atm H_2): δ 51 ppm (br s). Anal. Calcd: C, 39.15; H, 8.40; Cl, 6.42. Found: C, 39.94; H, 8.40; Cl, 6.66. IR (KBr in gas cell under H_2): ν_{M-H} 2204 (vw) and 2152 (m) cm^{-1} (deuteride ν_{M-D} 1568 (vw) and 1540 (m) cm^{-1}). As has been the case with previously isolated dihydrogen[2] complexes of iridium, no absorptions assignable to the H–H modes of **1** could be conclusively identified in comparison with the IR spectrum of the HD-substituted complex.

0020-1669/90/1329-0003$02.50/0

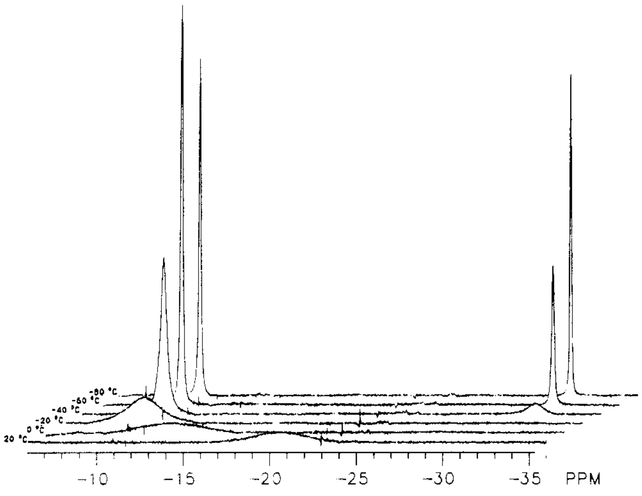

Figure 1. Variable-temperature ^1H NMR spectra (300 MHz) of the hydride region of $IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2$ dissolved in toluene-d_8 under 0.5 atm of H_2 (total pressure).

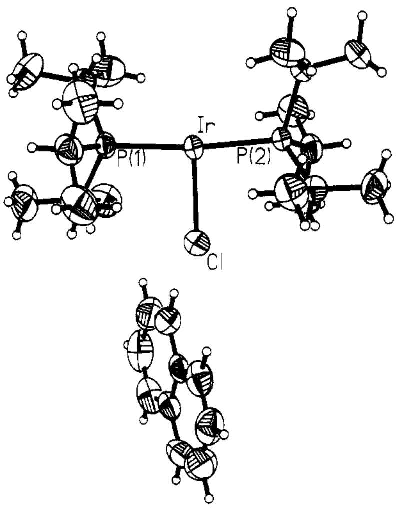

Figure 2. ORTEP projection of $IrH_2Cl(\eta^2\text{-}H_2)[P(i\text{-}Pr)_3]_2$. Selected bond lengths (Å): Ir–Cl = 2.427 (2); Ir–P(1) = 2.303 (1); Ir–P(2) = 2.307 (1). Hydrides on iridium were not located.

hydrogen pressure are obtained from samples of **2** under hydrogen pressure. These observations clearly demonstrate that the broad upfield resonance is due to rapidly exchanging metal-bound hydrogen and free hydrogen. This behavior contrasts with that of the cationic η^2-dihydrogen complexes[2,3] in CD_2Cl_2 solution for which exchange with free H_2 is not observable on the NMR time scale.

Variable-temperature ^1H NMR spectra of a sample of **1** under 0.5 atm of H_2 in toluene-d_8 are shown in Figure 1. Below −40 °C, separate resonances are clearly observed for the hydrides of **2** and the exchanging hydride and dihydrogen ligands[9] of **1** at −32.1 and −10.7 ppm respectively. The position of the equilibrium seen in Scheme I, as reflected by the relative intensities of these resonances, moves in the direction of **1** with increasing hydrogen pressure. Thus the hydride resonance of **2** is not observed at low temperatures for samples under 1 atm of H_2. The minimum T_1 value of 22 ms found[10] for the −10.7 ppm resonance at −60 °C clearly indicates the presence of a dihydrogen ligand[5] in **1**.[11] Between −20 and −60 °C, the width of the −10.7 ppm resonance decreases with decreasing temperature, but at −60 °C it remains too broad ($\nu_{1/2}$ = 32 Hz) for resolution of P–H coupling. Below −60 °C, the resonance broadens, reflecting a slowing of the exchange between the dihydrogen and hydride ligands of **1**.[12] However, the exchange remains fast on the NMR time scale to the −95 °C freezing limit of toluene-d_8.

The molecular structure of **1**·$C_{10}H_8$ was determined by a single-crystal X-ray diffraction study.[13] A room-temperature analysis yielded the positions of the $IrCl\{P(i\text{-}Pr)_3\}_2$ framework along the naphthalene of crystallization. An ORTEP diagram of the obtained structure is seen in Figure 2. The closest approach of the naphthalene molecule to the iridium center is 4.32 Å, clearly demonstrating the lack of a coordinative interaction. The Ir–Cl distance of 2.427 (2) Å is appreciably longer than the 2.31 Å sum of the atomic radii of the atoms or the 2.324 (5) Å distance found[14] for *trans*-$[IrCl_4(PPh_3)_2]^+$ and reflects the pronounced influence of a trans hydride ligand. The hydride ligands could not be reliably located.[15]

It is surprising that **1** is a η^2-dihydrogen complex that undergoes facile exchange with free H_2 while the closely related complex $IrH_5[P(i\text{-}Pr)_3]_2$ is a classical metal hydride complex with highly stabilized metal–hydrogen interactions.[1] Apparently, substitution of a hydride of $IrH_5[P(i\text{-}Pr)_3]_2$ with the weaker σ-donor chloride lowers the electron density at the iridium center as in the cationic η^2-dihydrogen complexes, such that the amount of charge transferred from the iridium center to the dihydrogen σ^*-antibonding orbital is within the limits in which a η^2-dihydrogen ligand is stabilized relative to a tautomeric dihydride.[16] Our NMR spectroscopic studies indicate that although the rate of exchange between the dihydrogen and hydride ligands in our neutral complex is similar to those of cationic iridium complexes containing dihydrogen and hydride ligands,[2,3] the elimination of hydrogen from the neutral complex is far more facile, reflecting a much weaker metal–dihydrogen interaction. Thus while the charge transfers from iridium to the dihydrogen σ^*-orbital are similar in the neutral and cationic complexes, the dihydrogen σ-donor interaction is apparently much weaker in the case of the neutral complex. Preliminary studies of the PCy_3 and $P(t\text{-}Bu)_3$ analogues of **1** have indicated that dynamic behavior similar to that of **1** is common to neutral iridium dihydrogen complexes. The elucidation of such general trends may result in increased predictability of the reactivity of iridium polyhydrides.

Acknowledgment. The support of this research by the Solar Energy Research Institute is gratefully acknowledged. We thank Prof. R. E. Cramer for his help in the X-ray diffraction studies.

Registry No. **1**, 124021-16-5; **1**·$C_{10}H_8$, 124021-17-6; **2**, 99920-04-4; H_2, 1333-74-0.

Supplementary Material Available: Tables of positional and thermal parameters and bond distances and angles (5 pages). Ordering information is given on any current masthead page.

---

(9) A resonance for free hydrogen at 4.60 ppm could not be conclusively identified due to signal broadening because of its involvement in the fluxional process and due to low signal intensity because of the low solubility of H_2 at lower temperatures.

(10) Measured by inversion–recovery with a 180–τ–90 pulse sequence.

(11) A minimum T_1 value of 98 ms, indicative[5] of a classical hydride, was found for the −32.1 ppm resonance at −60 °C.

(12) As a consequence of this high fluxionality, the −11 ppm resonance which is observed for a sample of **2** placed under 1 atm of HD shows no resolvable $^1J_{HD}$ at any temperature. The lack of an observable $^1J_{HD}$ in complexes containing highly fluxional dihydrogen and hydride ligands was reported previously in ref 2.

(13) Crystallographic data: triclinic $P\bar{1}$, $Z = 2$; a = 8.069 (3) Å, b = 13.822 (6) Å, c = 14.519 (5) Å, α = 82.56 (3)°, β = 82.34 (3)°, γ = 72.90 (3)°, V = 1527.0 (9) Å^3, ρ_{calcd} = 1.471 g/cm^3; μ = 45.60 cm^{-1}; Nicolet P3 diffractometer, Mo Kα radiation (λ = 0.71073 Å); 7784 independent reflections with 4° < 2θ < 45° collected, 7001 reflections used in refinement with $I > 3\sigma(I)$; R = 0.032, R_w = 0.031, GOF = 1.387.

(14) Aslanov, Mason, R.; Wheeler, A. G.; Whimp, P. O. *Chem. Commun.* **1970**, 30.

(15) A second X-ray analysis was performed at −100 °C. After all atoms except the hydride ligands were located and refined, a difference Fourier synthesis yielded four peaks with intensities of approximately 1 electron/Å^3. The peaks were located 1.3–1.5 Å from the iridium center, and two peaks were within 0.7 Å of each other. If the two close "hydrides" are viewed as a coordinated dihydrogen, an approximately octahedral geometry about the iridium center can be recognized. The peaks could not be refined.

(16) (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705-710. (b) Saillard, J. Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006-2026. (c) Jean, Y.; Eisenstein, O.; Volatron, F.; Maouche, B.; Sefta, F. *J. Am. Chem. Soc.* **1986**, *108*, 6587-6592. (d) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakoff, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* **1987**, *26*, 3054-3063.

Department of Chemistry
University of Hawaii
Honolulu, Hawaii 96822

Mario Mediati
Glen N. Tachibana
Craig M. Jensen*

Received September 7, 1989

Articles

Contribution from the University of Texas at Dallas,
P.O. Box 830688, Richardson, Texas 75083-0688

Potentiometry and NMR Studies of 1,5,9-Triazacyclododecane-*N*,*N*′,*N*″-triacetic Acid and Its Metal Ion Complexes

S. Cortes, E. Brucher,[†] C. F. G. C. Geraldes,[‡] and A. D. Sherry*

Received May 9, 1989

A new chelating macrocycle, 1,5,9-triazacyclododecane-*N*,*N*′,*N*″-triacetic acid (DOTRA), has been synthesized, and its complexes with Zn^{2+}, Cd^{2+}, Ca^{2+}, Mg^{2+}, and Mn^{2+} have been examined by potentiometry and NMR spectroscopy. The first protonation constant of the free ligand ($\log K_1 = 12.8$) was determined spectrophotometrically, while the remaining were evaluated from potentiometric data ($\log K_2 = 7.55$, $\log K_3 = 3.65$, $\log K_4 = 2.1$). DOTRA forms complexes with Mn^{2+}, Mg^{2+}, and Ca^{2+} rather slowly but reacts much more rapidly with Zn^{2+} and Cd^{2+}. As reported previously for the nine-membered-ring triaza analogue NOTA, DOTRA also forms a more stable complex with Mg^{2+} than with Ca^{2+} ($\log K_{st} = 7.1$ versus 6.0). High-resolution NMR spectra of the Zn^{2+}, Cd^{2+}, and Mg^{2+} complexes ($\log K_{st} = 19.0$, 15.7, and 7.1, respectively) indicate the three six-membered chelate rings are symmetrical and quite rigid in aqueous solution, as evidenced by nonequivalence of all six chelate ring protons.

Introduction

The complexation properties of the macrocyclic polyaza polycarboxylates have attracted considerable interest in recent years because the structural, equilibrium, and kinetic behavior of their metal ion complexes differ considerably from those of the analogous noncyclic polyamino polycarboxylates. Some of these ligands are also of practical importance, since their gadolinium(III) and manganese(II) complexes may be used as contrast agents for magnetic resonance imaging.[1,2] While several tetraaza tetracarboxylates have been prepared and investigated, the only triaza tricarboxylate reported so far is 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetic acid (H_3NOTA).[3] NOTA forms 1:1 complexes of high stability with a number of metal ions. Such complexes have been prepared with Al(III), Cr(III), Mn(II) and -(III), Fe(II) and -(III), Co(II) and -(III), Ni(II) and -(III), and Cu(II).[4-7] NOTA was found to be coordinated as a hexadentate ligand, and contrary to the complexes of the flexible EDTA, which often contain a H_2O molecule in the inner sphere (e.g. Mn^{2+}-(EDTA)(H_2O)[8]), the NOTA complexes with these ions are all six-coordinate. The geometry of several complexes investigated by X-ray diffraction was found to be distorted octahedral[5,7] (Cr(NOTA), Ni(NOTA)$^-$) or distorted prismatic[5] (Fe(NOTA), Cu(NOTA)$^-$) with a significant strain in the molecular framework.

The stability constants of the NOTA complexes are in general similar to those of EDTA.[3] A significant size selectivity was observed for the smaller Mg^{2+} ion, however. The stability constant of Mg(NOTA)$^-$ is higher[7,9] than that of Ca(NOTA)$^-$, while the complexes of Ca^{2+} with the larger tetraaza tetracarboxylates are all more stable than the corresponding Mg^{2+} complexes.[10] The structure of Mn(NOTA)$^-$ in solution is apparently similar to the solid-state structures described above, since NMRD studies of the relaxation rate of water protons in the solutions of Mn(NOTA)$^-$ indicate there are no inner-sphere water molecules.[2]

The relationship between the structure of these macrocycles (ring size, number of the five- versus six-membered chelate rings) and the thermodynamic and kinetic stability of their complexes is not well understood despite numerous investigations in this area. We have initiated the preparation and study of other triaza tricarboxylate macrocycles in an effort to further delineate these relationships and report here the acid-base and complexation properties of the new 12-membered-ring ligand 1,5,9-triazacyclododecanetriacetic acid (H_3DOTRA).

Experimental Section

Materials. All chemicals were of analytical grade and were used without further purification. Triazacyclododecane trihydrobromide was synthesized as described elsewhere.[11] Solutions of $ZnCl_2$, $CdCl_2$, $MnCl_2$, $CaCl_2$, and $MgCl_2$ were standardized complexometrically. The concentration of the DOTRA solution was also determined by complexometry using a standardized $CuCl_2$ solution and murexide as an indicator. KOH was standardized by potentiometric titration against potassium hydrogen phthalate[12] and stored under a N_2 atmosphere.

1,5,9-Triazacyclododecane. 1,5,9-Triazacyclododecane trihydrobromide (0.79 g, 1.91 mmol) was dissolved in 10 mL of water and the pH adjusted to 12 or higher using 5 M NaOH. The solution was concentrated to about 5 mL in vacuo and extracted with methylene chloride (3 × 5 mL). The organic extracts were combined, dried over NaOH pellets, and filtered. The solvent was evaporated in vacuo to leave the free amine as a yellow oil in 89% yield (0.29 g, 1.69 mmol): ^1H NMR ($CDCl_3$), δ 1.45 (p, 6 H), 2.55 (t, 12 H); ^{13}C NMR ($CDCl_3$), δ 26.23, 47.43.

1,5,9-Triazacyclododecane-1,5,9-triacetic Acid Trimethyl Ester. 1,5,9-Triazacyclododecane (0.076 g, 0.44 mmol) was dissolved in 5 mL

---

* To whom correspondence should be addressed.

[†] On leave from the Department of Inorganic and Analytical Chemistry, Lajos Kossuth University, H-4010, Debrecan 10, Hungary.

[‡] Permanent address: Department of Chemistry, University of Coimbra, 3000 Coimbra, Portugal.

(1) Desreux, J. F.; Barthelemy, P. P. *Nucl. Med. Biol.* **1988**, *15*, 9.
(2) Geraldes, C. F. G. C.; Sherry, A. D.; Brown, R. D., III; Koenig, S. H. *Magn. Reson. Med.* **1986**, *3*, 242.
(3) Hama, H.; Takamoto, S. *Nippon Kagaku Kaishi* **1975**, 1182.
(4) Takahashi, M.; Takamoto, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3413.
(5) Wieghardt, K.; Bossek, U.; Chandhuri, P.; Hermann, W.; Menke, B. C.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 4308.
(6) van der Merwe, M. F.; Boeyens, F. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 3489.
(7) van der Merwe, M. F.; Boeyens, F. C. A.; Hancock, R. D.; *Inorg. Chem.* **1985**, *24*, 1208.
(8) Richards, S.; Pedersen, B.; Silverton, F. U.; Hoard, F. L.; *Inorg. Chem.* **1964**, *3*, 27.
(9) Bevilacqua, A.; Gelb, R. T.; Hobard, W. B.; Zompa, L. F.; *Inorg. Chem.* **1987**, *26*, 2699.
(10) Delgado, R.; da Silva, F. F. R. F. *Talanta* **1982**, *29*, 815.
(11) Chavez, F.; Sherry, A. D. *J. Org. Chem.* **1989**, *54*, 2990.
(12) Gran, G. *Analyst* **1952**, *77*, 661.

0020-1669/90/1329-0005$02.50/0