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Communications

Unusual Photobehavior of *trans*-Dicyano(1,4,8,11-tetraazacyclotetradecane)rhodium(III) Perchlorate[1]

Sir:

The photobehavior of octahedral rhodium(III) complexes in room-temperature solution has received increasing attention in recent years.[2,3] Considerable evidence indicates that the ligand photosubstitution observed for these Rh(III) species on ligand field (LF) excitation originates from the low-lying triplet level $^3T_{1g}$.[2-4] Although d–d phosphorescence ($^3T_{1g} \rightarrow {}^1A_{1g}$) is also observed from this level, the detection of emission has generally been restricted to low-temperature measurements.[5-8] Recent studies have reported weak room-temperature *solution* emission for a series of Rh(III) acidopentaammine[9,10] and diacidotetraammine[11,12] species, but lifetimes are very short (in the 1–50-ns range). We report here the results of a photostudy of the compound *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$, where cyclam is the macrocyclic tetradentate amine ligand 1,4,8,11-tetraazacyclotetradecane.[13] To our knowledge the compound displays the strongest d–d phosphorescence signal ever reported for a Rh(III) complex under steady-state excitation conditions in room-temperature solution. In addition, the associated emission lifetime is 3 orders of magnitude longer than those found for other *trans*-diacidotetraammine systems.[14] The details of these observations are provided and discussed below.

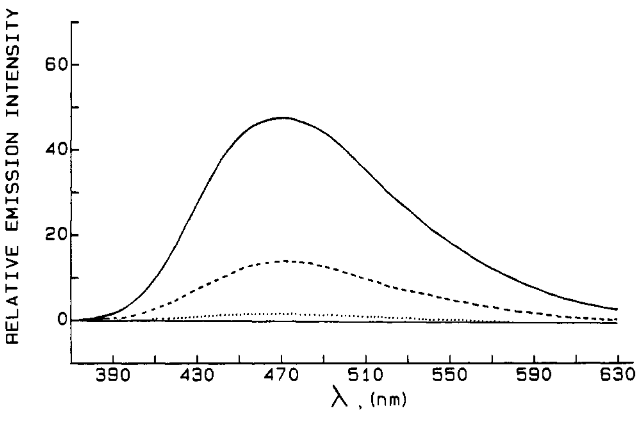

Figure 1. Steady-state emission spectra of a 1.4 × 10^{-3} M aqueous solution of *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ at 22 °C on 280-nm excitation: (—) pH 6.0 and 4.0; (---) pH 9.3; (···) pH 10.1.

When pure O_h symmetry is lowered to the D_{4h} symmetry present in *trans*-diacidotetraamine Rh(III) species, the reactive $^3T_{1g}$ excited state splits into ^3E_g and $^3A_{2g}$ levels. If the ^3E_g level is the lower-lying component, then ligands along the Z axis should be preferentially labilized,[16,17] as observed in the case of *trans*-Rh(NH$_3$)$_4$Cl$_2^+$ ($\phi_{Cl} = 0.13$, $\phi_{NH_3} < 10^{-3}$)[18] and related *trans*-diacido systems.[2] Alternatively, if the $^3A_{2g}$ excited state lies lower, photolabilization should be primarily restricted to the in-plane amine positions. At present no such cases have been reported in the literature. However, conditions appear especially favorable for a lower-lying $^3A_{2g}$ triplet component in *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$, where the axial cyanide ligands are both better σ donors and π acceptors than the in-plane amine ligand.[19] On the basis of our recent experience with the related Cr(III) species,[20] we were also hopeful that the presence of the macrocyclic ring would prevent cleavage of an individual Rh–amine bond and thus photoreactivity might be effectively eliminated altogether. Furthermore, since reaction and emission are competitive deactivation pathways for the triplet level, then reaction quenching might also be accompanied by a marked enhancement in the room-temperature phosphorescence lifetime and steady-state intensity. These expectations appear to have been realized.

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[1] Presented in part at the 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982.

[2] Ford, P. C.; Hintze, R. E.; Petersen, J. D. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; Chapter 5.

[3] Ford, P. C. *Coord. Chem. Rev.* **1982**, *44*, 61.

[4] Kelly, T. L.; Endicott, J. F. *J. Am. Chem. Soc.* **1972**, *94*, 278; *J. Phys. Chem.* **1972**, *76*, 1937.

[5] Thomas, T. R.; Crosby, G. A. *J. Mol. Spectrosc.* **1971**, *38*, 118.

[6] Thomas, T. R.; Watts, R. J.; Crosby, G. A. *J. Phys. Chem.* **1973**, *59*, 2123.

[7] DeArmond, M. K.; Hillis, J. E. *J. Chem. Phys.* **1971**, *54*, 2247.

[8] Hoggard, P. E.; Schmidtke, H. H. *Ber. Bunsenges. Phys. Chem.* **1973**, *77*, 1052.

[9] Bergkamp, M. A.; Brannon, J.; Magde, D.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1979**, *101*, 4549. Bergkamp, M. A.; Watts, R. J.; Ford, P. C. *J. Am. Chem. Soc.* **1980**, *102*, 2627.

[10] Adamson, A. W.; Fukuda, R. C.; Larson, M.; Mäcke, H.; Puaux, J. P. *Inorg. Chim. Acta* **1980**, *44*, L13.

[11] Sexton, D. A.; Skibsted, L. H.; Magde, D.; Ford, P. C. *J. Phys. Chem.* **1982**, *86*, 1758.

[12] Sexton, D. A.; Ford, P. C.; Magde, D. *J. Phys. Chem.* **1983**, *87*, 197.

[13] The complex was prepared according to: Kane-Maguire, N. A. P.; Miller, P. K.; Trzupek, L. S. *Inorg. Chim. Acta* **1983**, *76*, L179.

[14] Long-lived room-temperature d–d emission has been detected recently under pulse laser excitation for several Rh(III) complexes in the *solid* state.[15]

[15] Peterson, S. H.; Demas, J. N.; Kennelly, T.; Gafney, H.; Novak, D. P. *J. Phys. Chem.* **1979**, *83*, 2991.

[16] Incorvia, M. J.; Zink, J. T. *Inorg. Chem.* **1974**, *13*, 2489.

[17] Vanquickenborne, L. G.; Pierlott, K. *Inorg. Chem.* **1981**, *20*, 3673 and references therein.

[18] Kutal, C.; Adamson, A. W. *Inorg. Chem.* **1973**, *12*, 1454.

[19] Zinato, E.; Riccieri, P.; Prelati, M. *Inorg. Chem.* **1981**, *20*, L432.

[20] Kane-Maguire, N. A. P.; Crippen, W. S.; Miller, P. K. *Inorg. Chem.* **1983**, *22*, 696.

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Table I. Solution and Glass Phosphorescence Lifetimes (τ)[a] for *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ and Some Nonmacrocyclic Systems

compd	temp, K	τ_{H_2O}	τ_{Me_2SO}	τ_{DMF}	ref
t-Rh(cyclam)(CN)$_2^+$ [b]	326.1	2.0			*c*
	315.6	3.1			*c*
	305.6	4.9			*c*
	295.6	8.0	16.0	16.7	*c*
	285.4	13.9			*c*
	77		189	292	*c*
t-Rh(NH$_3$)$_4$Cl$_2^+$	298	0.002			*d*
	77	10.8			*e*
t-Rh(NH$_3$)$_4$Br$_2^+$	298	0.002			*d, f*
t-Rh(py)$_4$Br$_2^+$	77	464			*g*

[a] Lifetimes are in μs and are the average of at least two determinations. [b] All solutions are approximately 0.005 M in nitric acid. The lifetime shows no discernible dependence on complex concentration in aqueous solution. The very limited solubility of the complex in Me$_2$SO and DMF precluded such a study in these solvents. [c] This work. [d] Reference 12. [e] Reference 5, water–methanol glass. [f] Reference 11. [g] Reference 6, water–methanol glass.

LF photolysis (296 and 306 nm)[21] were carried out on 0.001 M HNO$_3$ solutions of the title compound with use of an Oriel 1-kW Hg–Xe arc lamp and optical train described elsewhere.[22] Cyclam release was monitored via solution pH changes, while a CN$^-$-selective electrode (Sensorex 521 CN) was used for CN$^-$ loss measurements. Even following extended photolysis no substitution photochemistry was detected: $\phi_{\text{cyclam}} \leq 10^{-4}$ and $\phi_{CN^-} \leq 10^{-4}$.

Steady-state emission spectra near room temperature were obtained with an Aminco-Bowman spectrophotofluorimeter.[20] A Corning CS 0-51 or CS 0-52 filter was placed just in front of the photomultiplier tube to eliminate second-order grating phenomena. Strong, broad, structureless emission consistent with $^3A_{2g} \rightarrow {}^1A_{1g}$ phosphorescence was observed centered at 470 nm following 280- or 313-nm excitation of air-saturated solutions of the title compound in water, dimethyl sulfoxide (Me$_2$SO), and dimethylformamide (DMF). Although the 470-nm emission maximum is at considerably higher energy than values previously reported for Rh(III) d–d phosphorescence, the finding is consistent with trends in complex ligand field strengths.[5,23] The emission half-width, $\nu_{1/2}$, at 298 K in aqueous solution (4.7 × 10^3 cm^{-1}) is similar to those reported for halopentaammines under comparable conditions.[9] The emission intensity was essentially unaffected by the presence of dissolved oxygen. Importantly, the emission was totally quenched in strongly basic solution (pH >11) and regenerated on reacidification (Figure 1). This sensitivity to base is in accord with prior observations by Adamson and co-workers of base quenching of Rh(NH$_3$)$_5$Cl^{2+} emission[10] and with data for Cr(III) amine systems containing N–H protons.[24,25] It is very unlikely that impurities are responsible for these observations, since the same emission was observed for samples of *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ from different syntheses, and the signal remained unchanged after several recrystallizations from aqueous solution. Furthermore, at 77 K, where most Rh(III) complexes emit, the emission signal intensified but remained centered at 470 cm.

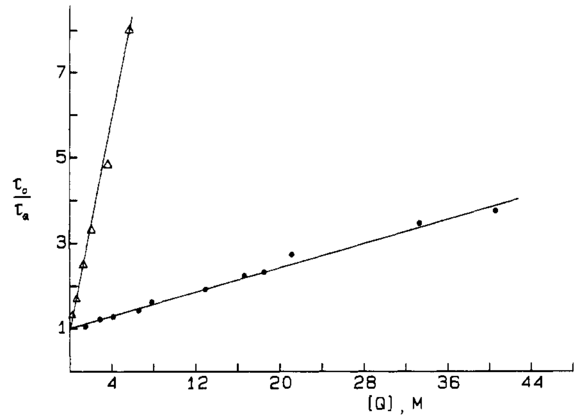

Figure 2. Stern–Volmer plot of OH$^-$ and Cr(CN)$_6^{3-}$ quenching of an aqueous *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ solution at 22 °C: (△) OH$^-$ quenching, [Q] = 10^5[OH$^-$]; (●) Cr(CN)$_6^{3-}$ quenching, [Q] = 10^4[Cr(CN)$_6^{3-}$] (pH 5.9, ionic strength 0.5).

Emission lifetimes of *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ near room temperature and 77 K were determined with use of a 250-kW N$_2$ laser (Molectron UV-12) via procedures described previously.[20] Emission at 470 nm exhibited single-exponential decay, which on analysis yielded the lifetime results presented in Table I. The corresponding data for some nonmacrocyclic *trans*-diacidotetraammine systems are also included for comparison purposes. It is clear that the lifetime of the title compound in room-temperature solution is dramatically lengthened relative to those of the nonmacrocyclic complexes, while the 77 K values more closely correspond. These results are consistent with the argument that lifetime lengthening in *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ is primarily associated with elimination of room-temperature reaction out of the $^3A_{2g}$ excited state. However, the analogous complexes *trans*-Rh(NH$_3$)$_4$(CN)$_2^+$ and *trans*-Rh(en)$_2$(CN)$_2^+$ have not as yet been reported. Thus the relative importance of cyclam restraints in reducing photoreactivity and increasing lifetimes is not at present clearly defined.[26]

An Arrhenius plot of the lifetime temperature dependence of *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ in aqueous solution over the range 12.3–53.0 °C (using data from Table I) yielded an apparent activation energy of 9.0 ± 0.2 kcal mol^{-1}. A thermally activated process such as $^3A_{2g} \rightsquigarrow {}^3E_g$ back internal conversion may be responsible in part for these temperature observations. The steady-state emission intensity quenching noted earlier in basic solution (Figure 1) is accompanied by a corresponding decrease in the emission lifetime. From the slope of the Stern–Volmer plot (Figure 2) a bimolecular quenching rate constant, k_q, of 1.6 × 10^{10} M^{-1} s^{-1} was obtained at 22 °C. This value corresponds closely to that reported earlier by Adamson and co-workers for base quenching of Rh(NH$_3$)$_5$Cl^{2+} and approximates that expected for a diffusion-controlled process. Finally, we note that the unusually long $^3A_{2g}$ lifetime of *trans*-Rh(cyclam)(CN)$_2^+$ coupled with its strong phosphorescence and photoinertness open up interesting prospects for its utilization in energy-transfer and electron-transfer studies. We find for example that the emission is quenched by added Cr(CN)$_6^{3-}$ in aqueous solution with a rate constant, k_q, at 22 °C of 9.4 × 10^7 M^{-1} s^{-1} (Figure

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(21) Absorption maxima of *trans*-[Rh(cyclam)(CN)$_2$]ClO$_4$ in aqueous solution are at 267 and 218 nm with molar absorptivities of 270 and 1620, respectively.[13]

(22) Kane-Maguire, N. A. P.; Allen, M. M.; Vaught, J. M.; Hallock, J. S.; Heatherington, A. L. *Inorg. Chem.*, in press.

(23) For example, the emission maxima for *trans*-Rh(NH$_3$)$_4$Br$_2^+$, Rh(NH$_3$)$_5$Cl^{2+}, and Rh(NH$_3$)$_6^{3+}$ are at 747, 668, and 612 nm, respectively.[5,11] In addition, the macrocyclic ring may minimize distortion in the equilibrated triplet level and thus reduce the emission Stoke shift below nonmacrocyclic values.

(24) Langford, C. H.; Tipping, L. *Can. J. Chem.* **1972**, *50*, 887.

(25) Kane-Maguire, N. A. P.; Phifer, J. E.; Toney, C. G. *Inorg. Chem.* **1976**, *15*, 593.

(26) Kutal and Adamson[18] have previously shown macrocyclic ligand effects to be small in *trans*-Rh(cyclam)Cl$_2^+$ relative to that for the corresponding Cr(III) species.[27] However, *trans*-Rh(cyclam)Cl$_2^+$ differs importantly from *trans*-[Rh(cyclam)(CN)$_2^+$ in that the lowest lying triplet excited-state component in the former compound is ^3E_g, for which *Z*-axis photolabilization (i.e. Cl$^-$ release) is anticipated and observed.[18]

(27) Kutal, C.; Adamson, A. W. *Inorg. Chem.* **1973**, *12*, 1990.

2). The actual modes of this and other quenching phenomena are presently under more detailed investigation.

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Department of Chemistry
Furman University
Greenville, South Carolina 29613

D. B. Miller
P. K. Miller
N. A. P. Kane-Maguire*

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Bis(allyl)nickel and Bis(pentadienyl)iron as Precursors for the Synthesis of $Ni(PF_3)_4$, $Ni(PF_2H)_4$, and $Fe(PF_3)_5$

Sir:

The synthesis of PF_3 complexes of transition metals is known to be significantly more difficult than the synthesis of metal carbonyls,[1,2] although well-defined processes for preparations of compounds such as $Ni(PF_3)_4$, $Fe(PF_3)_5$, $Cr(PF_3)_6$, etc. have been reported.[2–4] Wilkinson[2] first fluorinated $Ni(PCl_3)_4$ with antimony trifluoride to get the PF_3 complex. Timms[4] used the metal atom reactor technique to prepare $Ni(PF_3)_4$ (85% yield). Clark and Brimm[5] allowed $Ni(CO)_4$ to react with PF_3 in a pressure vessel at 150 °C for 12 h and obtained 90% pure $Ni(PF_3)_4$ by displacement of CO. A number of other procedures based on the reaction of nickel metal and PF_3 at high temperatures (up to 100 °C) and high pressures (50–350 atm), with reaction times of up to 10 days, have been reported[6] to give good yields. Most procedures using nickel and PF_3 under milder conditions and short reaction times have given low yields,[7] although studies in this laboratory, with H_2S-activated nickel and $H_3B{\cdot}PF_3$ as a source of PF_3, have shown that yields of up to 98% can be obtained with use of low PF_3 pressures (2 atm H_3BPF_3) and temperatures of 50 °C for 46 h.[1] $Ni(PF_3)_4$ can also be prepared in ca. 20% yield from nickelocene and PF_3.[8]

While $Ni(PF_3)_4$ and related species can be prepared with some difficulty by the above procedures, the compound $Ni(PF_2H)_4$ has been successfully prepared only by utilizing the metal atom reactor.[9] Other methods, useful for preparing $Ni(PF_3)_4$, were not successful for the PF_2H analogue.

$Fe(PF_3)_5$ was first prepared by Kruck and Prasch by the direct reaction of FeI_2 and PF_3 over copper powder.[3] The iron–PF_3 complex has also been prepared in 25% yield with use of metal atom cocondensation techniques.[4] However, the synthesis of $Fe(PF_3)_5$ is usually carried out by the displacement of CO from $Fe(CO)_5$ by PF_3. High pressures of PF_3 give only partially substituted products: ultraviolet irradiation of $Fe(CO)_2(PF_3)_3$ and excess PF_3 is necessary to obtain $Fe(PF_3)_5$.[10] Separation procedures are quite involved.

Herein we report an effective synthetic route to tetrakis(trifluorophosphine)nickel and related species, to pentakis(trifluorophosphine)iron, and to the elusive tetrakis(difluorophosphine)nickel. The procedures represent modifications and extensions of the work of Wilke and Bogdanovic, which involved $Ni(allyl)_2$ and organophosphines.[11] We have thus prepared $Ni(PCl_3)_4$, $Ni(PF_3)_4$, $Ni(PF_2N(CH_3)_2)_4$, $Ni(PF_2Cl)_4$, and $Ni(PF_2H)_4$ through the reaction of $Ni(allyl)_2$ with the appropriate ligand. The experimental procedures are quite convenient; reactions are carried out at 25 °C, at pressures below 1 atm, and with reaction times of approximately 1 h. For all of the preparations, the pure nickel complexes can be isolated from the unidentified organic byproducts by vacuum line trap-to-trap distillation or by recrystallization. The synthesis of the iron–PF_3 complex was carried out with bis(pentadienyl)iron (an "open ferrocene") and PF_3. The displacement process goes smoothly, but the procedure is handicapped by present difficulties in preparing the bis(pentadienyl)iron starting material in large quantity.

Standard vacuum line procedures as described by Shriver[12] were used throughout. Bis(η^3-allyl)nickel was prepared from the reaction of allylmagnesium chloride with nickel bromide in ether as described by Wilke and Bogdanovic.[11] PF_2H was prepared by the method of Centofanti and Rudolph,[13] and PF_3 was a purified sample from Ozark-Mahoning. Bis(pentadienyl)iron was prepared as described by Wilson, Ernst, and Cymbaluk.[14]

Synthesis of $Ni(PF_3)_4$ and Related Species

In a trap with Teflon stopcocks, a 4.39-mmol sample of PF_3 (29% excess) was condensed onto a 0.85-mmol sample of $Ni(allyl)_2$. The reagents were then allowed to react without solvent at 25 °C. After 1.5 h, the reaction mixture was fractionated. A 0.49-mmol sample (58% yield) of $Ni(PF_3)_4$ was recovered in the –80 °C trap. IR, and ^{31}P and ^{19}F NMR spectra coincided with the reported literature values.[9]

In reactions similar to that described above, a 70% yield of $Ni(PF_2Cl)_4$ was isolated by fractionation under high vacuum; an excellent yield of $Ni(PCl_3)_4$ was easily obtained and crystallized, and a quantitative yield of white crystalline $Ni[PF_2N(CH_3)_2]_4$ was recovered. The products were identified by NMR spectroscopy and by their physical characteristics.[4,9,15,16] In addition to the previously reported data for $Ni(PF_2Cl)_4$ and $Ni[PF_2N(CH_3)_2]_4$, ^{31}P NMR shifts of +177.6 and +169 ppm respectively were observed (downfield from H_3PO_4).

Synthesis of $Ni(PF_2H)_4$

A 1.25-mmol sample of PF_2H (0.8% excess) was condensed onto 0.31 mmol of $Ni(allyl)_2$ in a 9-mm NMR reaction tube, equipped with a gas expansion bulb and a stopcock. The reaction, carried out at a temperature of –80 to –90 °C for about 1 h, was monitored by ^{31}P, ^{19}F, and ^{1}H NMR. ^{19}F and ^{31}P spectra agree with those obtained previously in this laboratory.[9] The ^{31}P spectrum indicated a 50% yield of Ni(P-

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(1) Montemayor, R. G.; Parry, R. W. *Inorg. Chem.* **1979**, *18*, 1470.
(2) Wilkinson, G. *J. Am. Chem. Soc.* **1951**, *73*, 5501.
(3) Kruck, Th.; Prasch, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 754. Clark, R. J. *Inorg. Chem.* **1964**, *3*, 1395.
(4) Timms, P. L. *J. Chem. Soc. A* **1970**, 2526.
(5) Clark, R. J.; Brimm, E. O. *Inorg. Chem.* **1965**, *4*, 651.
(6) Kruck, Th.; Baur, K. *Chem. Ber.* **1965**, *98*, 3070. Nixon, J. F.; Sexton, M. D. *J. Chem. Soc. A* **1969**, 1089.
(7) Street, G. B.; Burg, A. B. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 47.
(8) Nixon, J. F. *Chem. Commun.* **1966**, 34; *J. Chem. Soc. A* **1967**, 1136.
(9) Staplin, D. C.; Parry, R. W. *Inorg. Chem.* **1979**, *18*, 1473.
(10) Kruck, Th. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 53.
(11) Wilke, G.; Bogdanovic, B. *Angew. Chem.* **1961**, *73*, 756.
(12) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.
(13) Centofanti, L.; Rudolph, R. W. *Inorg. Synth.* **1970**, *12*, 281.
(14) Wilson, D. R.; Ernst, D. R.; Cymbaluk, T. H. *Organometallics* **1983**, *2*, 1220.
(15) Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. *Top. Phosphorus Chem.* **1967**, *5* (Chapter 4).
(16) Schmutzler, R. *Inorg. Chem.* **1964**, *3*, 415. Kruck, Th.; et al. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 522.

0020-1669/83/1322-3833$01.50/0