reduction of O_2 forming free O_2^-, which upon dismutation is converted to HO• and trapped by alcohol, and (3) dissociation of O_2^- from the inner-sphere complex. The latter two explanations would not account for the absence of HO–DMPO• trapping in the absence of the ethanol mediator. Therefore, these reactions must be inner sphere with coordinated O_2^- generating trappable radicals from substrates within the solvent cage.

Conclusion

Whenever HO• is formed during the reduction of H_2O_2 (inner sphere) or O_2 (outer sphere), the DMPO or DMPO/alcohol trapping systems detect the appropriate radicals as have been characterized for the $Ti(edta)(H_2O)^-/H_2O_2$ system and the $Ru(NH_3)_6^{2+}/O_2$ system. When O_2 reductions occur by inner-sphere pathways, the DMPO trapping shows a much lower yield or no detectable radical signal for the early transition-metal reductants. Unless a large pool of reducing agent is present, the superoxo intermediate $[Fe(edta)O_2]^{2-}$ may oxidize its own edta ligand in a small fraction of events, competitively with further reduction of the coordinated O_2^- complex. The attack of O_2^- on the ligand chelate system can be transferred to a more active sacrificial agent in the solvent cage such as DTT or ascorbate. This latter effect may be important in the Dervan-type DNA-nicking drugs,[23,32] which contain a $Fe(edta)^{2-}$ group tethered to a methidium intercalator or other DNA-sequence-specific binding agents. The present study shows that dithiothrietol rapidly reduces the $Fe(edta)(O_2)^{2-}$ intermediate to the Fe(III) peroxo complex. The 1e reduction of this complex should yield a pool of HO• while a 2e reduction yields a ferryl–oxo intermediate. These would be generated at a slow rate in the vicinity of a receptive DNA substrate to suffer nicking. The results found here for the additional $Ru(NH_3)_6^{2+}$, $Ti(edta)(H_2O)^-$, and $Fe(edta)^{2-}$ reductants show that the DMPO spin trap is a useful probe as to whether an inorganic autoxidation process occurs by an inner- or outer-sphere pathway. Absence of significant amounts of the HO–DMPO• adduct can be taken as evidence of an inner-sphere process in which coordinated O_2^- is further reduced by additional reducing equivalents of the reductant. In some cases, small amounts of radicals derived from attack of the ligand structure by O_2^- coordinated within the cage can also be deduced, leading to useful mechanistic information in conjunction with separate experiments involving the reactivity of free O_2^- or HO• and the free ligand.

Acknowledgment. This work was supported by the National Science Foundation through NSF Grant CHE-8417751 and by the donors of the Petroleum Research Fund, Administered by the American Chemical Society.

Registry No. DMPO, 40936-29-6; PBN, 3376-24-7; $Ti^{III}(edta)(H_2O)^-$, 74111-14-1; $Fe^{II}(edta)^{2-}$, 15651-72-6; $Ti(H_2O)_6^{3+}$, 17524-20-8; $Fe(H_2O)_6^{2+}$, 15365-81-8; $Ru(NH_3)_6^{2+}$, 19052-44-9; CH_3CH_2OH, 64-17-5; CH_3OH, 67-56-1; $(CH_3)_2CO$, 67-64-1; $(CH_3)_3COH$, 75-65-0; H_2O_2, 7722-84-1; O_2, 7782-44-7; O_2^-, 11062-77-4; HO•, 3352-57-6.

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Synthesis of $Cr(tacn)X_3$ Compounds (tacn = 1,4,7-Triazacyclononane). Photochemistry and Emission Properties of the Triisothiocyanate

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Received August 21, 1987

A series of $Cr(tacn)X_3$ compounds, where tacn = 1,4,7-triazacyclononane, has been prepared and characterized for X = Br, F, CN, and NCS. The latter two compounds emit in room-temperature solutions and were therefore explored as candidates for sensitization and quenching studies. The triisothiocyanate compound appears to be the most promising. Although it is insoluble in water, it dissolves in a number of nonaqueous solvents, emits strongly at 753 nm with a lifetime at 298 K of 27 μs in dmso, is quenched efficiently by a number of metal ions and complexes as well as by oxygen, and is thermally stable and relatively photostable, having a quantum yield for thiocyanate photosubstitution of about 0.05 in dmso, dmf, and acetonitrile. The emission of the compound is quenched by $Cr(en)_3^{3+}$, with a rate that is consistent with thermally activated energy transfer. Photolysis in aerated dmso of the triisothiocyanate leads to increased emission from the complex, a result of oxygen scavenging.

Introduction

There continues to be considerble interest in energy- and electron-transfer processes involving the excited states of transition-metal ions.[1-3] Analogous processes are involved in a number of important chemical and biological processes.

Research activity in this general area has included a large number of studies of energy transfer to and from chromium complexes.[4] These are particularly important to our understanding because of the well-defined spectroscopy of the chromium(III) quartet and doublet states,[5] which provide a system archetypal for many other less tractable systems. Studies of energy transfer involving chromium complexes are often hampered, however, by effects arising from the charges on the complexes, as well as by the high photolability of many of the molecules used to date.[6-8] The first of these problems can be particularly severe in studies in nonaqueous solvents, an unfortunate feature because these are otherwise excellent media in which to study the sensitization and quenching interactions between ground and excited states of organic molecules and metal complexes.[9]

It therefore appeared to us to be potentially useful to develop a series of uncharged Cr(III) complexes in which the overall ligand field and therefore the excited-state energy levels could be varied and to study their emission and photochemistry. This was in the hope that some useful new uncharged quenchers and sensitizers would emerge, compounds that would be useful in energy-transfer and quenching studies as well as interesting in their own photochemistry and photophysics. A promising candidate series was the triacido complexes of the tridentate ligand 1,4,7-triazacyclononane (tacn);[10] it was our expectation, based on current models of Cr(III) photochemistry,[11] that these molecules would be reasonably photostable, particularly where the acido ligand was of

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(1) Balzani, V.; Scandola, F. *J. Chem. Educ.* **1983**, *60*, 314.
(2) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(3) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.
(4) Balzani, V.; Moggi, L.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *75*, 321.
(5) Forster, L. S. *Transition Met. Chem.* (*N.Y.*) **1969**, *5*, 1.
(6) Ballardini, R.; Gandolfi, M. T.; Balzani, V. *Inorg. Chem.* **1987**, 26, 862.
(7) White, H. S.; Becker, W. G.; Bard, A. J. *J. Phys. Chem.* **1984**, *88*, 1840.
(8) Frank, R.; Rau, H. *J. Phys. Chem.* **1983**, *87*, 5181.
(9) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219.
(10) Zompa, L. J.; Young, R. *Inorg. Chem.* **1976**, *15*, 1499.
(11) Vanquickenborne, L. G.; Ceulemans, A. *Coord. Chem. Rev.* **1983**, *48*, 157.

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Table I. Elemental Analysis, UV–Visible, Phosphorescence, and Selected IR Spectral Data for Cr(tacn)X_3 Compounds

		elemental anal.					UV/vis spectrum				
X		% C	% H	% N	% X	%Cr	L_2, nm (ϵ)	L_1, nm (ϵ)	calcd	phos, nm	IR spectrum ν, cm^{-1} (assignt)
F	found	25.7	6.0	14.8		18	394 (25)	544 (68)	542		436 (w), 504 (s) (Cr–N); 520 (s), 550 (s), 595 (w) (Cr–F)
	calcd	30.3	6.35	17.6	23.9	21.8					
Br	found	16.3	3.62	9.3	51.9	10.9	460	614	596		456 (m) (Cr–N); 295 (m) (Cr–Br)
	calcd	17.1	3.56	9.97	57.0	12.4					
CN	found	41.8	5.80	32.0		20.2	332 (80)	420 (67)	416	742[a]	406 (s), 457 (s) (Cr–N); 339 (s), 374 (m) (Cr–C); 540 (w) (Cr–C–N)
	calcd	41.7	5.79	32.4		20.0					
NCS	found	30.1	4.23	22.4	25.5[b]		396 (88)	503 (175)	509	753[c]	444 (m), 458 (m) (Cr–N); 480 (w) (δ(NCS)); 790 (w), 830 (w) (C–S); 2050 (s) (C–N)
	calcd	30.4	4.25	23.6	27.1						
dmso							407 (50)	547 (110)	549[d]		

[a] Main peak; has a shoulder at 725 nm and a small peak at 758 nm. [b] Here X = S; Cr interferes with the S analysis. [c] Main peak; there are subsidiary peaks at 715 and 772 nm. [d] Based on the ligand field strength given for dmf.[11]

lower photolability than the nonane nitrogen ligand. This assumes that because of its multidentate nature and probable rigidity in the stable coordinated conformation, there is little likelihood of photolabilization of the nonane ligand, an assumption strongly supported by the observation of the photostability[12] of Cr(tacn)$_2^{3+}$.

In this paper we report the preparation and properties of some members of this series of compounds.

Experimental Section

Preparation of Compounds. Except where noted, the elemental analyses, UV–visible, and infrared spectral data for the compounds below are given in Table I.

Cr(tacn)(CO)$_3$. According to the procedure of Chaudhari et al.[13] 1.05 g of Cr(CO)$_6$ and 0.616 g of nonane[10] were dissolved in 100 mL of mesitylene (Aldrich) and gently refluxed under nitrogen for 3 h. The yellow solid that precipitated was filtered from the cooled solution by using a fine sintered-glass disk and was washed twice with 50-mL portions of benzene, ethanol, and ether. The compound showed the CO absorptions at 1880 and 1700–1740 cm^{-1} reported[13] and was not further characterized.

Perhaps due to higher humidity in this laboratory environment, the Cr(tacn)(CO)$_3$ product was not as air stable as stated by the original authors. The product slowly reddened on the surface on exposure to air and light, so precautions were taken to prevent any decomposition of the product during handling. In addition, it was observed that during reflux, chromium carbonyl collected in the condenser to a considerable extent, necessitating its periodic return to the solution and lowering the yield of the product considerably from the 60–80% reported. In subsequent preparations a 2-fold excess of chromium carbonyl was added, which markedly improved the observed yield; the excess chromium carbonyl was easy to recover after the preparation was over.

Cr(tacn)Br$_3$. This new compound was prepared analogously to the dtne compound described by Wieghardt et al.[14] A 0.5-g sample of Cr(tacn)(CO)$_3$ (1.8 × 10^{-3} mol) was refluxed in 50 mL of CHCl$_3$ (Spectral grade, Mallinckrodt) under a nitrogen atmosphere and 5 g of liquid bromine added dropwise over 5 h. The green precipitate that formed was filtered off by using a fine sintered-glass filter and washed with 50 mL of each of chloroform and ether. The yield was 0.7 g, 90% of theoretical.

The compound is insoluble in chloroform, water, dmf, thf, and methylene chloride but dissolves to some extent in dmso. The solution in dmso slowly turns magenta, more rapidly on heating, as does a suspension in water. The dry solid is stable to air and light. The compound showed no weight loss on heating at 60 °C for 24 h.

Cr(tacn)(CN)$_3$. A solution of 0.30 g (7 × 10^{-4} mol) of Cr(tacn)Br$_3$ in 6 mL of dmso (Aldrich, spectral grade, dried over molecular sieves) was heated at 60 °C for 30 min under nitrogen. To the resulting magenta solution of the tris(dimethyl sulfoxide) complex was added 1.0 g of finely ground sodium cyanide (2 × 10^{-2} mol) and the mixture stirred at 80 °C for 3 h, followed by cooling to room temperature. The yellow product was filtered off, washed with ethanol and ether, and dried. The remaining mother liquor was heated on a hot plate to reduce the volume and a further quantity of the yellow compound subsequently obtained, filtered, and cleaned as above. The total yield was 0.12 g (65%).

The compound is insoluble in dmso, chloroform, carbon tetrachloride, methyl chloride, and acetonitrile but is sparingly soluble in water. The bright yellow material was recrystallized from warm water.

Cr(tacn)(NCS)$_3$. A solution containing 0.1 g (2.4 × 10^{-4} mol) of Cr(tacn)Br$_3$ in 6 mL of dmso was solvolyzed at 65 °C for 60 min, and 0.25 g (3 × 10^{-3} mol) of NaNCS (Aldrich) was added, followed by heating at 70 °C for 75 min. After cooling, 15 mL of water was added to the resulting red solution and the red precipitate filtered off, washed with ether, and dried. The yield was 65 mg (60%). Additional product could be obtained by heating the mother liquor in a petri dish at 80 °C to reduce the volume, followed by reprecipitation by addition of water. This increased the overall yield to about 85%.

The compound is soluble in acetone, dmso, dmf, acetonitrile, thf, and pyridine but insoluble in water.

Cr(tacn)F$_3$. As in the previous two syntheses, a solution of 100 mg (0.24 mmol) of the tribromide was solvolyzed in 20 mL of dmso and subsequently anated with 0.1 g (2.4 mmol) of solid sodium fluoride. After the unreacted solid sodium fluoride was filtered off, precipitation with 45 mL of ether/5 mL of acetone gave a red oil. The solid derived from this oil by workup had a UV–vis spectrum in aqueous solution which had bands at 384 and 516 nm, different from expectation (542 nm), for the trifluoride and which, on adding base, red-shifted in the manner familiar for aquo complexes. This method therefore resulted in only partially anated products that formed aquo complexes on solution in water.

An authentic, but impure, sample of the trifluoro compound was prepared by the reaction in dmso of 0.26 g of Cr(tacn)Br$_3$ with 0.75 g of silver fluoride. The mixture was heated at about 60 °C until precipitation of silver salt was complete. The precipitated silver salt was filtered off, and 0.1 g of solid product was obtained by precipitation from the cooled solution by acetone/ether addition. The yield was 70% of theoretical. Addition of chloride to an aqueous solution of the compound resulted in a colloidal precipitate of silver chloride, revealing residual contamination of this product. This probably does not seriously influence most of the data obtained but leads to low analytical figures and molar absorptivities and may well have resulted in emission quenching.

The trifluoro compound is insoluble in thf, dmf, dmso, and nitromethane but dissolves in water and formamide.

Photochemical Studies. Samples were dissolved in the appropriate solvent to give a suitable absorbance (about 0.3) at the desired irradiation wavelength. These were irradiated with either a 150-W Hanovia xenon arc lamp in combination with Bausch and Lomb high-intensity monochromator and 20-cm water infrared and Corning 4-96 blue filters or with the unfiltered but beam-expanded (about 6-mm diameter) beam of 488-nm radiation from a Spectra-Physics 6-W argon ion laser used at powers up to 100 mW. Incident light intensities were determined by using the potassium reineckate actinometer[15] and, in the case of the xenon lamp, monitored for constant intensity by following the emission from a standard solution of Ru(bpy)$_3^{2+}$. The extent of photoreaction was followed by chromatographic analysis, which revealed both product formation and reactant disappearance, and by direct chemical analysis for thiocyanate.[15] In some experiments, loss of emission intensity was also used, as discussed later.

Emission Measurements. Emission spectral and intensity measurements were made by using a Jarrell-Ash 0.25-m monochromator preceded by a Corning 3-71 red filter and a 1-cm path of concentrated potassium dichromate solution to remove light shorter than about 650 nm in wavelength. The detector was a cooled (−30 °C) RCA 31034 photomultiplier feeding into a modified Keithley 410 electrometer interfaced to a PDP-11 computer. Together with a stepper motor-driven buret (Gilmont 0.2 mL), this equipment also allowed the semiautomated recording of Stern–Volmer quenching plots. Emission lifetimes were

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(12) Ditze, A.; Wasgestian, F. *J. Phys. Chem.* **1985**, *89*, 426.

(13) Chaudhuri, P.; Wieghardt, K.; Tsai, Y.; Kruegar, C. *Inorg. Chem.* **1984**, *23*, 427.

(14) Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.

(15) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

measured by using a time-correlated single-photon-counting apparatus previously described[16] as well as by using a nitrogen laser[17]/monochromator/Hamamatsu R928 photomultiplier/Tektronix 2445 oscilloscope system.

Chromatographic Analyses. Good separations of reactant and product complex peaks were obtained by using reverse-phase high-pressure liquid chromatography as described elsewhere.[18] The eluents used were 25 mM in sodium butanesulfonate as ion interaction reagent and 25 mM in triethylamine hydrochloride as competing ion, dissolved in water and in 93% methanol. The best separations were obtained by using a 50% isocratic combination of these two eluents. Peaks were detected by their UV–vis absorptions at suitable wavelengths in the range 260–320 nm.

Analyses. Elemental analyses were performed by Canadian Microanalytical Services, except for the chromium analysis, which was carried out as follows. A 5–10-mg sample of the complex was digested on a hot plate with 1 mL of 50% HNO_3 at about 90 °C until the solution had become green. After this mixture was cooled, 2 mL of organo-pure water, three pellets of sodium hydroxide, and 10 drops of 30% hydrogen peroxide were added, and the solution was again digested at 90 °C until it was clear and bright yellow. The cooled solution was made up to 100 mL with organo-pure water and the absorbance of chromate measured at 373 nm ($\epsilon = 4.82 \times 10^3$ L mol^{-1} cm^{-1}).

Thiocyanate Analysis. Free thiocyanate in photolyzed, thermalized, or standard solutions was determined by means of the formation and absorbance of the red iron(III)/thiocyanate complex. Because of the influence of the nonaqueous solvent present, it was necessary to standardize the method for each solvent system used. Typically, to 2.5 mL of the photolyzed nonaqueous solution was added 5 mL of developer (0.1 M $Fe(NO_3)_3$ in 0.1 M $HClO_4$) and the solution made up to 25 mL with water. Any precipitate of unreacted starting complex that formed was filtered off with a 0.22-μm filter. The absorbance was measured in a 1-cm cell at the usual wavelength of 460 nm in the initial experiments. This band maximum was observed to shift with solvent, however, and in dmso, Fe^{3+} complexes also absorb and interfere. For the quantum yield measurements, therefore, the absorbance at the maximum of the 510-nm band was used. This is free from such interference.[19] The molar absorptivity values (L mol^{-1} cm^{-1}) observed and used for the various solvents were as follows: dmso, $\epsilon_{456} = 3.16 \times 10^3$, $\epsilon_{510} = 2.16 \times 10^3$; dmf, $\epsilon_{460} = 3.42 \times 10^3$, $\epsilon_{510} = 1.98 \times 10^3$; acetonitrile, $\epsilon_{460} = 3.88 \times 10^3$ (10 mL of Fe^{3+} developer was used); tetrahydrofuran interfered and no color developed. In several runs the technique was checked for linearity and accuracy by standard additions of thiocyanate to the test solution with a microliter syringe. These tests were uniformly satisfactory.

Results

Table I summarizes the data that support the identity of the complexes synthesized. The elemental analyses of the Cr(tacn)X$_3$ complexes for X = Br, CN, NCS, and F are generally satisfactory although the bromide, which was fortunately only an intermediate, gives low analyses except for hydrogen. The UV–vis absorption spectra (Table I) lie in the regions to be expected. Thus, there is good agreement between the position of the lowest ligand field quartet band and the value calculated from published D_q values[11] by the assumption of quasi-O_h symmetry using the average values for the two ligands present,[20] given in the "calcd" column of Table I. The table also lists selected non-nonane infrared bands and their assignments.[21] These are again consistent with the given structures.

The only probable structural ambiguity that might occur in this set of compounds is in the bonding of the thiocyanate ligand. As Table I shows, the bands observed at 480 cm^{-1} (δ(NCS)) and at 790 and 830 cm^{-1} (ν(C–S), N-bonded) and the absence of bands in the range 690–720 cm^{1} (ν(C–S), S-bonded) show that the ligand is N-bonded,[21] consistent with the situation for most other chromium(III) thiocyanate complexes.

The complexes as a group tend to be rather insoluble. This was not completely unexpected but is nevertheless disappointing, as it restricts the study of the photochemistry and photophysics and the utility of the compounds. The tribromide and triisothiocyanate are soluble to some extent in dmso, and the latter is also somewhat soluble in acetonitrile, pyridine, thf, and dmf. While the triisothiocyanate is completely insoluble in water, the latter is the sole pure solvent we have found for the tricyanide and it is still only slightly soluble. This was a disappointment, as we had anticipated that the cyanide complex would be one of the better candidates for energy transfer and sensitization studies. It turns out, however, that the isothiocyanate is superior.

The investigation of the emission properties of the compounds showed that, whereas the tribromide and trifluoride did not emit significantly, room-temperature aqueous solutions of the tricyanide emitted at a wavelength of 742 nm. The triisothiocyanate emits, independently of the solvent, at 753 nm with subsidiary bands at 715 and 772 nm. The room-temperature emission from the compound was unusually intense for a chromium complex in solution. The emission yield was estimated by comparing the spectra of 380-nm absorbance-matched solutions of this complex in dmso and $Cr(en)_2(NCS)_2^+$ in acidic aqueous solution. The latter emits with a quantum yield of 8.6×10^{-4} over essentially the same wavelength range,[22] obviating the need for wavelength sensitivity corrections. The ratio of the integrated areas under the two emission spectra was found to be 5.5 in favor of the triisothiocyanate, and this leads to a quantum yield of emission in an aerated 298 K solution of 0.005, among the higher values observed for a chromium complex. This promising observation and the solubility difficulties with the tricyanide prompted a switch in focus to the thiocyanate compound.

The emission from the triisothiocyanate is quenched by the oxygen present in solution. Degassing of a dmso solution with nitrogen resulted in an increase by a factor of 2.1 in the emission intensity; consistent with this, the emission lifetime was measured to be 27 μs in degassed solution and 12 μs in aerated dmso. The doublet state of this compound is also quenched by Fe^{3+}, Ag^+, $Cr(CN)_6^{3-}$, and $Cr(en)_3^{3+}$. For *tert*-butylammonium hexacyanochromate, a linear Stern–Volmer plot is obtained for the quenching in degassed dmso, with $K_{SV} = 4.8 \times 10^3$ M^{-1}. With a lifetime of 27 μs, this gives a collisional quenching rate constant of 1.8×10^8 L mol^{-1} s^{-1}, significantly lower than diffusion controlled. Of even more interest is the observation that the emission is quenched by $Cr(en)_3^{3+}$ with a $K_{SV} = 128$ M^{-1} and therefore a k_q of 4.7×10^6 L mol^{-1} s^{-1}.

In the various solvents used, thermal decomposition of the triisothiocyanate was slow, only 1–2% of free thiocyanate being found to have been released on standing overnight at room temperature in the dark in dmso or dmf solution. This gives a crude estimate of the first-order rate constant for thiocyanate loss of about 2×10^{-7} s^{-1} at room temperature. At 60 °C, about 30% of the thiocyanate was released in 135 min in dmf solution; the chromatographic analyses discussed later showed that the thiocyanate loss was a sequential process, complicating the interpretation of the thiocyanate release. For this same solution the emission intensity from the triisothiocyanate starting material had decreased by only 12%; this supports loss of between two and three thiocyanates per molecule in the thermal reaction under these conditions.

On irradiation of aerated or degassed solutions of the complex in dmso, dmf, or acetonitrile, free thiocyanate was again found. Chromatographic analysis of the products formed was particularly clear-cut when dmso was the solvent. As shown in Figure 1, an unphotolyzed solution of the starting complex gave (A1) a single peak eluting after 6 min. On irradiation with 100 mW of 488-nm radiation for 3 min (A2), a new peak appeared at 5.2 min while the peak for the starting complex decreased in size. At 5-min irradiation (A3), the starting material had declined further, the peak at 5.2 min had grown somewhat, and a third peak at 3.5 min had appeared. At overall radiation times of 7 (A4), 9, 13, (not shown), and 20 (A5) min, the starting peak continued to decrease while the peak at 5.2 min remained roughly constant and that at 3.5 min continued to increase.

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(16) Stuart, D. C.; Kirk, A. D. *Rev. Sci. Instrum.* **1977**, *48*, 186.

(17) Nagata, I.; Kimura, Y. *J. Phys. E* **1973**, *6*, 1193.

(18) Hewavitharana, A.; Kirk, A. D. *Anal. Chem.*, in press.

(19) Cusumano, M.; Langford, C. H. *Can. J. Chem.* **1978**, *17*, 2222.

(20) Ballhausen, C. J. *Introduction to Ligand Field Theory*; McGraw-Hill: New York, 1962; p 107.

(21) Nakomoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978.

(22) Kirk, A. D.; Porter, G. B. *J. Phys. Chem.* **1980**, *84*, 887.

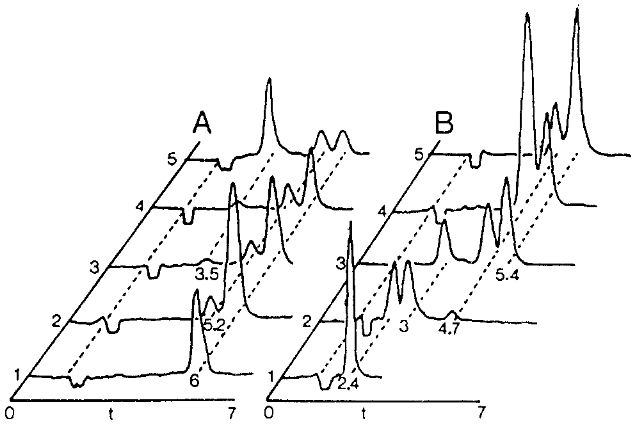

Figure 1. Chromatography of photolyzed dmso solutions of Cr(tacn)$(NCS)_3$ and thiocyanate-anated solutions of Cr(tacn)$(dmso)_3^{3+}$. Elution times in minutes are indicated at the ends of the dashed lines. Part A: Photolysis of Cr(tacn)$(NCS)_3$, 100-mW, 488-nm radiation; A1, unphotolyzed; A2, 3-min photolysis; A3, 5-min photolysis; A4, 7-min photolysis; A5, 20-min photolysis. Part B: Anation of Cr(tacn)$(dmso)_3^{3+}$ by thiocyanate; B1, initial solution; B2, NCS^- added, solution not heated; B3, solution heated at 70 °C for 20 min; B4, solution further heated at 80 °C for 60 min; B5, photolyzed Cr(tacn)$(NCS)_3$.

During this sequence of irradiations the UV–vis spectral changes were monitored and thiocyanate analyses performed. The latter showed that thiocyanate was being released. Spectral changes occurred also; as irradiation proceeded, the band at 504 nm steadily moved toward the red and decreased in intensity. Initially there appeared to be an isosbestic point at 528 nm, but this crossing point of the spectra moved steadily to the red, being closer to 538 nm after 30-min photolysis. The band at 388 nm did not shift but steadily decreased in intensity.

The spectral changes for the main band are as to be expected for successive replacements of the stronger field isothiocyanate ligand by weaker dmso. The results also show that secondary photolysis is significant despite the lower absorbance of the initial photoproduct at the irradiation wavelength of 488 nm evidenced by the decrease in absorption on irradiation. This requires that the quantum yields of the successive photolysis steps are as large or larger than that of the first. Similar results were obtained either with rapid (laser) or slow (xenon lamp) photolysis so that thermal reactions were not of major importance.

The elution order for the product peaks implied by the previous results was unusual; in this method[18] peaks usually elute in order of increasing, not decreasing, charge. To confirm the implied reverse assignment (mono-, di-, and triisothiocyanate in order of elution), the thermal anation by thiocyanate of a solution of the Cr(tacn)$(dmso)_3^{3+}$ was used to prepare the same peaks thermally. Figure 1 also shows the chromatogram (B1) of a dmso solution of the tribromide compound thermalized to equilibrium and showing the spectrum of the tris(dimethyl sulfoxide) compound given in Table I; there is a single chromotographic peak at 2.4 min. When sodium thiocyanate was added to this solution, there was a rapid blue shift in the lowest energy visible absorption band, consistent with thiocyanate substitution, and the chromatogram (B2) showed three peaks, two of equal size at 2.5 and 3.0 min and a small peak at 4.7 min. The solution was then heated for 20 min at 70 °C. This resulted in a further blue shift of the absorption band to 510 nm with an increase in intensity; in the chromatogram (B3) the peak at 4.7 min was very large, the peaks at 2.5 and 3.0 min were small, and a new peak appeared at 5.4 min. On reheating at 80 °C for 60 min, a further small blue spectral shift occurred and the chromatographic peaks (B4) at 4.7 and 5.4 min increased at the expense of the others. To confirm that the 5.4-min peak was the triisothiocyanate despite its shorter retention time, a photolyzed solution of this compound was again run (B5) and gave a small peak at 4.5 min and a large peak at 5.2 min. This shows that the retention times in the anation experiments are all shorter than in the photolysis study owing to the slightly differen elution conditions (fresh eluents had been made up) and allows the assignment of the peak sequence as Cr(tacn)$(dmso)_3^{3+}$, Cr(tacn)$(dmso)_2NCS^{2+}$, Cr(tacn)(dmso)$(NCS)_2^+$, Cr(tacn)$(NCS)_3$. It is likely that in these complexes effects of hydrophobicity are dominating the behavior, leading to this unusual sequence. We plan to study the chromatographic aspects of this separately.

A study of the photochemistry in dmf led to similar results and behavior. In this solvent, however, the thermal solvolysis of the tribromide and subsequent thiocyanate anation appeared to be more complex (possibly owing to formation of mixed dmf/Br/NCS mono(1,4,7-triazacyclononane) complexes) so that a completely unambiguous assignment of all the chromatographic peaks was not possible. Nevertheless, up to 10-min of photolysis time with 100 mW of 488-nm radiation, only a single product peak is seen to grow in the chromatogram; during this period thiocyanate is released into the solution and, in contrast to the behavior in dmso, the lowest energy visible absorption band increases in intensity while exhibiting a red shift as before. These results suggest the simple photosubstitution of a single thiocyanate is the predominant initial process in dmf, just as in dmso.

Measurement of the quantum yield for thiocyanate release in nitrogen-degassed solutions gave the value 0.05 in both dmf and dmso. In an aerated solution of acetonitrile the quantum yield was 0.02. Since about 50% of the doublet state is quenched by the equilibrium concentration of oxygen in aerated acetonitrile, this implies a value of 0.04 if most of the reaction occurs via the doublet state.

In most solvents studied, the equilibrium concentration of oxygen caused a decrease in emission intensity by a factor of about 2, consistent with the reduction in lifetime mentioned earlier. On photolysis in aerated solution in dmf, thf, acetonitrile, etc., the emission intensity declined with irradiation time, as is to be expected for the loss of the emitting starting complex. In dmso, however, the unexpected and initially puzzling result of an increase in emission intensity with time occurred, up to a factor of almost 2, followed by a slow decrease back to or below the original value if photolysis was discontinued. Addition of hydrogen ion, ferric ion, or silver ion to scavenge the released thiocyanate was without effect on the rate of the thermal "back-reaction", although ferric and silver ions were observed to be efficient emission quenchers. Addition of thiocyanate or water after photolysis led to an instantaneous reduction of the enhanced emission down to the initial value or lower. Finally, photolysis of a degassed solution in dmso led only to a decrease in the emission intensity. These observations show that there is no production of a new emitting species which returns to starting complex via a thermal back-reaction but that in dmso, oxygen is being scavenged from the solution during photolysis.

Discussion

While the new complexes described here are all strictly speaking C_{3v} in the coordination microsymmetry around the central Cr(III) ion, from the point of view of the ligand field theory, they can be considered as quasi-O_h species.[20] This allows a simple calculation of the wavelength expected for the lowest energy quartet/quartet absorption band based on the average ligand field strength on each axis, and as Table I shows, this agrees very satisfactorily with observation. The angular-overlap model[23] also allows a calculation of the labilization expected for each of these complexes and a summary of the calculations is given in Table II. This shows that, assuming that the nonane ligand will not be labilized by virtue of its multidentate nature and probable rigidity, the tricyanide and trifluoride are expected to be completely photostable while the bromide and isothiocyanate are borderline cases where the difference in excited-state bond strengths for the two modes is quite small although still in the same direction as the others. The photochemistry of the first three compounds has not yet been investigated, but this study of the triisothiocyanate shows that it photolyzes thiocyanate only with a small quantum

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(23) Vanquickenborne, L. G.; Ceulemans, A. *J. Am. Chem. Soc.* **1977**, *99*, 2208.

Table II. Calculation of Excited-State Bond Strengths[a] for Cr(tacn)X_3 Compounds

X	bond strength, μm^{-1} Cr–N	bond strength, μm^{-1} Cr–X	diff, kJ mol^{-1}	ligand loss predicted
F	0.898	1.46	196	nonane
Br	0.898	0.890	0.9	Br^-
CN	0.898	1.09	23	nonane
NCS	0.898	0.916	2.1	nonane

[a] Based on the ligand field parameters for ammonia and X ligands given in ref 11.

yield, 0.05, relatively independent of solvent, in agreement with theoretical expectations that this should be the minor mode of reaction.

This complex, being thermally and relatively photostable and emitting efficiently with a long doublet lifetime, meets well the criteria of this study and will be a useful addition to the available quenching and energy-transfer species. It is noteworthy that in degassed solution the emission yield is 0.01, a value that compares very favorably with 0.002 in dmso for *trans*-Cr(cyclam)$(NH_3)_2^+$[24] and that approaches the 0.034 for Ru$(bpy)_3^{2+}$.[22]

Consistent with its long lifetime, the molecule is quenched by oxygen, ferric and silver ions, and the complexes $Cr(CN)_6^{3-}$ and $Cr(en)_3^{3+}$. The last case is interesting in that the doublet energy of the acceptor is higher than that of the donor, 1.49[25] and about 1.39 μm^{-1}, respectively (the latter value is estimated from the onset of emission and is approximate). The most likely explanation of this is an uphill, thermally activated process, although other mechanisms are conceivable. The given doublet energies show that energy transfer in this direction must overcome a Boltzmann factor of 0.008 at 298 K. It is to be noted that this is not inconsistent with the ratio of the bimolecular quenching constants for the two complex ions studied, 0.03, the first of which is for conventional, exothermic energy transfer but is slower than expected for the diffusion-controlled process. Energy-transfer quenching should lead to sensitized emission, but this could not be observed owing to the much more efficient emission from the unquenched donor complex. We intend to pursue these aspects further in a future study.

The quenching by silver and ferric ions is unlikely to occur either by energy or electron transfer. A possible mechanism is binding to the free S end of the coordinated isothiocyanate; this would perturb the excited doublet state and may well catalyze intersystem crossing to the ground state.

The scavenging of oxygen on photolysis of aerated dmso solutions is an interesting phenomenon. Two mechanisms might be considered: redox reaction with dmso of the doublet excited state of the complex, arising because of its greater oxidation potential, or energy transfer to produce singlet oxygen, which then reacts with dmso or impurities such as dimethyl sulfide. Of these two possibilities the second seems more likely, on the basis of the uniqueness to dmso of the process and the known reactivity of singlet oxygen with dimethyl sulfide.[26]

These results show that this molecule fulfills the criteria that we set out to meet. It is sufficiently thermally and photochemically stable to allow energy-transfer studies. It has a doublet state of long lifetime that can be quenched by a number of metal ions, complexes, and other species such as molecular oxygen. This implies in turn its potential utility as a sensitizer of low-energy excited states. Since the molecule is neutral and soluble in nonaqueous solvents, it allows the possibility of quenching and sensitization studies without the complexities associated with ionic species in nonaqueous media.

Acknowledgment. The authors wish to thank the University of Victoria and The Natural Sciences and Engineering Research Council of Canada for financial support. Dr. A. McAuley kindly provided us with an initial sample of the tacn ligand, and D. Kneeland, W. Riske, T. Ward, and P. A. Warren generously assisted with various aspects of the experiments.

Registry No. Cr(tacn)$(CO)_3$, 88253-23-0; Cr(tacn)Br_3, 112421-66-6; Cr(tacn)$(CN)_3$, 112421-67-7; Cr(tacn)$(NCS)_3$, 112421-68-8; Cr(tacn)F_3, 112421-69-9; Br_2, 7726-95-6; O_2, 7782-44-7; Fe^{3+}, 20074-52-6; Ag^+, 14701-21-4; $Cr(CN)_6^{3-}$, 14875-14-0; $Cr(en)_3^{3+}$, 15276-13-8; dmso, 67-68-5; dmf, 68-12-2; Cr(tacn)$(dmso)_3^{3+}$, 112421-70-2.

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[24] Kane–Maguire, N. A. P.; Wallace, K. C.; Miller, D. B. *Inorg. Chem.* **1985**, *24*, 597.

[25] Forster, L. S.; Moensted, O. *J. Phys. Chem.* **1986**, *90*, 5131.

[26] Schenck, G. O. *Chem. Ber.* **1963**, *96*, 517.

Notes

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Relevance of the Acid–Base Phosphorane/Phosphoranide Equilibrium to the Tautomeric Phosphorane/Phosphine Equilibrium in the Action of an Activated Ketone on Tetracyclic Tetraaminophosphoranes

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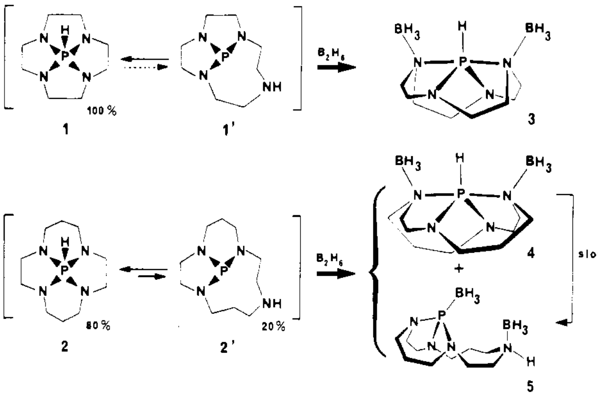
Received August 13, 1987

We recently reported the unexpected difference in behavior of cyclenphosphorane **1** and cyclamphosphorane **2** toward the same Lewis acid, B_2H_6[1] (Scheme I). Compound **1** was found to react readily with diborane to yield the bis adduct **3** in which no rearrangement of the initial structure has occurred whereas **2**, which is known to be in equilibrium with an open form in solution, led to a mixture of closed cyclamphosphorane–bis(borane) **4**, analogous to **3**, and an open cyclamphosphine–bis(borane) **5**.

Scheme I. Reactivity of **1** and **2** toward Diborane



In this paper, we have investigated the reactivity of **1** and **2** toward an activated ketone, trifluoroacetophenone (**6**), in order (i) to reveal a possible open tautomeric form for **1**, (ii) to know whether **2** reacts as a phosphorane or a phosphine toward the ketone, and (iii) to evaluate the part of the NH site in the open form.

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[1] (a) Dupart, J.-M.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1983**, *105*, 1051. (b) Dupart, J.-M.; Grand, A.; Pace, S.; Riess, J. G. *Inorg. Chem.* **1984**, *23*, 3776. (c) Dupart, J.-M.; Le Borgne, G.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc.* **1985**, *107*, 1202.