Coordination Chemistry Reviews, 111 (1991) 153–160
Elsevier Science Publishers B.V., Amsterdam

Pressure Effects on Bimolecular Excited States Processes

Peter C. Ford and Daniel R. Crane

Department of Chemistry, University of California
Santa Barbara, CA 93106 USA

Abstract

Summarized are recent studies concerned with the use of hydrostatic pressure to probe bimolecular mechanisms for the deactivation of transition metal complex excited states. These include investigations of Brønsted base quenching of rhodium(III) amine ligand field states, Lewis base quenching of the metal-to-ligand charge transfer state of $Cu(dmp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline), reactive quenching by various organic substrates of the long-lived $\sigma^* \rightarrow \sigma^b$ state of the platinum dimer $Pt_2(\mu-\eta^2-H_2P_2O_5)_4^{4-}$ and the competitive electron transfer and energy transfer quenching of the MLCT excited state of the copper(I) complex $Cu(dpp)_2^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) by various substrates.

Introduction

The use of hydrostatic pressure allows for the systematic and continuous variation of solution properties as a probe of excited state energies and mechanisms [1-3]. Earlier studies in this laboratory (some in collaboration with others) have used pressure (0.1 to 400 MPa) to probe the "unimolecular" deactivation mechanisms of the electronic excited states (ES) of various transition metal complexes including ligand substitution and isomerization reactions as well as nonradiative and radiative deactivation to the ground state (GS) [4-9]. Our more recent emphasis has been on bimolecular pathways such as ES quenching by electronic energy transfer and by chemical processes such as electron transfer, atom transfer or proton transfer as well as by excited state complex ("exciplex") formation. The experiments described here are concerned with evaluating the resulting effects on the dynamics of the bimolecular quenching of luminescent metal complex ES.

The quenching constants k_q were determined according to

$$k_q = (\tau_e^{-1} - \tau_o^{-1})[Q]^{-1} \qquad (1)$$

where τ_e and τ_o are the measured lifetimes of the luminescent ES in the presence and absence of quencher Q, respectively, under otherwise identical conditions. The volume of activation for any dynamic process is defined by

0010-8545/91/$03.50

$$\Delta V^{\ddagger}_{i} \;=\; -RT\left(\frac{d \ln k_i}{dP}\right)_T \tag{2}$$

where k_i is the rate constant at a particular pressure. In general, the sign and magnitude of a $\Delta V^{\ddagger}_{i}$ may reflect changes in intrinsic volumes of the reactants and/or in solvation volumes (especially if there is creation or depletion of charged species), but it should be noted that the term "volume of activation" is a convenient representation of pressure effects and should not be overinterpreted as solely indicating actual volume changes along a reaction coordinate. The $\Delta V^{\ddagger}_{q}$ values described here were determined from the slopes of plots of $\ln(k_q/k_q{}^a)$ vs P at constant T, where $k_q{}^a$ and k_q are the quenching rate constants measured at ambient pressure and at pressure P, respectively, calculated according to Eq. 1 with concentrations corrected for solvent compressibility. These plots were linear (within experimental uncertainty) for the pressure ranges investigated (e.g., Figure 1); however, it should also be noted that second order effects may indeed lead to nonlinear behavior [10].

Brønsted Base Quenching of Rhodium(III) Amines Ligand Field States

The *trans*-Rh(cyclam)$(CN)_2{}^+$ ion (**I**, cyclam = 1,4,8,11-tetraazacyclotetradecane) displays luminescence from a ligand field excited state (${}^3LF^*$) in room temperature, aqueous solution with a lifetime (8.1μs) [11] several orders of magnitude longer than generally observed for rhodium(III) amine complexes [12]. As has been observed for some other Rh(III) amines , the ${}^3LF^*$ emission from **I** is quenched by OH^- in solution (Eq. 3), a process attributed to amine deprotonation [13]. The rates for this process approach the diffusion limit ($k_3 = 10^{10}\ M^{-1}\ s^{-1}$) [11,13]. The pressure effect on k_3 and on the rate constant for similar quenching of the ${}^3LF^*$ emission from $Rh(ND_3)_6{}^{3+}$ (by OD^- in D_2O) have been examined in this laboratory [14]. The resulting $\Delta V^{\ddagger}_{q}$ values were positive, $+4.1 \pm 0.5$ and $+4.0 \pm 0.6\ cm^3\ mol^{-1}$, respectively. In these cases positive $\Delta V^{\ddagger}_{q}$'s would be predicted by two factors. For reactions which approach diffusion limiting rates, positive $\Delta V^{\ddagger}$'s are often seen owing to the increased viscosity of the solvent under pressure. However, the relative incompressibility of water makes this contribution very small ($< 1\ cm^3\ mol^{-1}$) [15]. Of much greater impact would be desolvation of the ions, hence a postitive contribution to $\Delta V^{\ddagger}_{q}$, accompanying the charge neutralization resulting from proton transfer from the LF ES of the rhodium cations to OH^-. The change in partial molar volumes $\Delta\bar{V}$ would be quite large for complete proton transfer (the $\Delta\bar{V}$ between OH^- and H_2O is ~ $+16\ cm^3\ mol^{-1}$ and desolvation of the complex ion should give a comparably large and positive $\Delta\bar{V}$ as well [1]). Thus, the much smaller value of $\Delta V^{\ddagger}_{q}$ likely reflects a very early transition state for the proton transfer process leading to ES quenching. Such a result is certainly not unexpected given the k_q values near the diffusion limit in aqueous solution.

$${}^3[\textit{trans}\text{-Rh(cyclam)(CN)}_2{}^+]^* \xrightarrow{k_3[OH^-]} \textit{trans}\text{-Rh(cyclam)(CN)}_2{}^+ \tag{3}$$

Quenching of [$Pt_2(POP)_4{}^{4-}$]* by H-Atom Abstraction from Benzylic Substrates

The d^8-d^8 dimer of platinum(II) $Pt_2(\mu\text{-}\eta^2\text{-}H_2P_2O_5)_4{}^{4-}$ (subsequently denoted as Pt_2) displays strong, long-lived phosphorescence with $\tau_m \sim 10$ μs and $\phi_r = 0.55$ moles/einstein in aqueous solution [16]. The luminescent excited state $^3Pt_2{}^*$ is quenched by substates such as benzylic alcohols and ethers, main group hydrides and halocarbons [17] from which atom abstraction can occur readily and has been shown to be active in the photodehydrogenation of alcohols to the homologous ketone (Eq. 4) [18]. The manner by which Pt_2H_2 in Eq. 4 forms is uncertain, but the monohydride species Pt_2H has been demonstrated to form under conditions relevant to the photodehydrogenation, and atom abstraction to give an organic free radical plus a Pt(II)-Pt(III) mixed valence dimer (e.g. Eq. 5) is considered to be the probable first step.

$$Pt_2{}^* + PhCH(OH)CH_3 \longrightarrow H_2Pt_2 + PhC(O)CH_3 \qquad (4)$$

$$Pt_2{}^* + R\text{-}H \longrightarrow HPt_2{}^{\bullet} + R^{\bullet} \qquad (5)$$

The effect of pressure on the quenching of phosphorescence from $Pt_2{}^*$ was examined in this laboratory [19] for a series of benzylic substrates and the relevant $\Delta V^{\ddagger}q$ data are summarized in Table 1. In each case, the rates for these relatively slow quenching processes are enhanced by higher pressure (i.e., $\Delta V^{\ddagger}_q$'s are negative). Furthermore, although a kinetic isotope effect (k_h/k_d) of 3.6 is apparent for deuterium replacement of the benzylic hydrogen of α-methylbenzyl alcohol, the $\Delta V^{\ddagger}_q$ values for the protio and deuterio substrates are experimentally indistinguishable. Notably, activation parameters determined by Harvey [20] from the temperature dependence of k_q show that the rates are largely governed by the negative entropies with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$

Table 1: Volumes of Activation Measured for the Quenching of $^3Pt_2{}^*$ in CH_3OH by Benzylic Quenchers ($\Delta V^{\ddagger}$ values in $cm^3\ mol^{-1}$)^a

Quencher	$\Delta V^{\ddagger}_q$($cm^3\ mol^{-1}$)^b	k_q, L $mol^{-1}s^{-1}$ ^{c}
$C_6H_5CH_2OH$	-5.4	1.6×10^6
$(C_6H_5)_2CHOH$	-2.8	7.1×10^5
$C_6H_5CH(OH)C_2H_5$	-2.6	4.6×10^5
$C_6H_5CH(OH)CH_3$	-4.4	9.4×10^5
$C_6H_5CD(OH)CH_3$	-4.7	2.6×10^5
$C_6H_5CH_2\text{-}O\text{-}CH_3$	-4.1	1.4×10^6

a 21± 1°C
b estimated uncertainty is < ± 1 cm^3mol^{-1}
c k_q at ambient pressure

equal to +2.4 kcal mol^{-1} and -19 eu, respectively, for benzyl alcohol, and +1.6 kcal mol^{-1} and -26 eu for α-methylbenzyl alcohol. The substantially negative $\Delta S^{\ddagger}_q$ values are consistent with the negative $\Delta V^{\ddagger}_q$ values for these two substrates and point to significant organization in the formation of the transition state for the step leading to quenching and the associated hydrogen atom. These results would be consistent with a transition state formed by an associative interaction between the benzylic H-atom donor and a site on the excited state complex $^3Pt_2^*$, presumably one of the metal atoms.

Lewis Base Quenching of [Cu(dmp)$_2^+$]* by Excited State Complex Formation

The copper(I) complex Cu(dmp)$_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) displays metal to ligand charge transfer (MLCT) luminescence in ambient temperature CH_2Cl_2 solutions [21]. This emission has been shown to be quenched by various Lewis bases B and the reaction of B with the MLCT state $^3I^*$ at the metal center to give "exciplex" formation has been proposed as the responsible mechanism (Scheme I) [21]. The viability of this mechanism was tested in this laboratory by comparing, in the presence and absence of Lewis base quenchers, the pressure effects on the emission lifetimes of Cu(dmp)$_2^+$ with those on the emission lifetimes of the analogous 2,9-diphenyl-1,10-phenanthroline (dpp) complex Cu(dpp)$_2^+$ [22]. Lewis base quenching of the latter species is much less significant, apparently because the much bulkier phenyl substituents are more effective in blocking the copper center from increasing its coordination number.

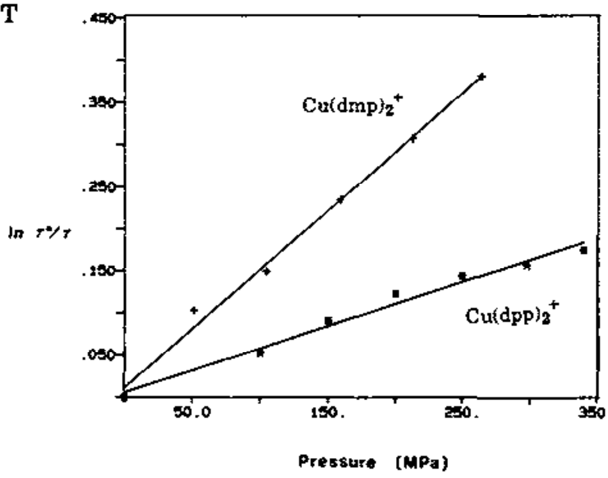
Scheme I

$$\begin{tikzcd}
{[Cu(dmp)_2^+]^*} \arrow[r, shift left, "K_b[B]"] \arrow[d, "k_n + k_r" right, "-h\nu" left] & {[Cu(dmp)_2{:}B^+]^*} \arrow[l, shift left] \arrow[d, "k_n''"] \\
Cu(dmp)_2^+ & {[Cu(dmp)_2{:}B^+]} \arrow[l, "-B", "fast"']
\end{tikzcd}$$

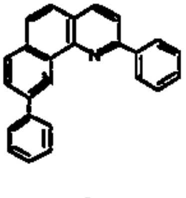
The application of pressure to CH_2Cl_2 solutions of either Cu(dmp)$_2^+$ or Cu(dpp)$_2^+$ led to systematic decreases in the emission lifetimes even in the absence of added Lewis bases (Figure 1). However, it is clear from the ln(τ^0/τ) vs P plots of Fig. 1 that the emission lifetimes of [Cu(dmp)$_2^+$]*are significantly the more pressure sensitive. In the absence of quencher, $\tau = k_d^{-1}$, where k_d is the sum of the radiative (k_r), unimolecular reaction (k_p) and nonradiative (k_n) rate constants for ES deactivation. For [Cu(dmp)$_2^+$]* and [Cu(dpp)$_2^+$]*, the emission quantum yields at ambient temperature are small (<10^{-3}) and unimolecular photoreactions are not observed. Thus, the dominant deactivation pathway is nonradiative and the pressure sensitivity of τ reflects that of the various nonradiative deactivation pathways. From Figure 1 the respective $\Delta V^{\ddagger}_n$ values of -3.4 and -1.6 cm^3 mol^{-1} were determined for $[Cu(dmp)_2^+]^*$ and $[Cu(dpp)_2^+]^*$ [22]. The small negative value for $[Cu(dpp)_2^+]^*$ is within the range of those seen for other metal complexes decaying nonradiatively via a unimolecular weak coupling mechanism [1,8]. The more negative $\Delta V^{\ddagger}_n$ for $[Cu(dmp)_2^+]^*$ is outside this range and suggests participation of an associative pathway as one component of the the nonradiative deactivation of this less sterically crowded complex, i.e. that the k_n pathway in this case may involve formation of a solvent complex with the ES prior to nonradiative decay.

The differences between the ES properties of these two complex ions were further accentuated when Lewis base quenchers were present. The presence of 0.30 M CH_3OH or CH_3CN in the CH_2Cl_2 solutions shortened the ambient pressure and temperature emission lifetime of $[Cu(dmp)_2^+]^*$ from 90 ns to 66 ns or 63 ns, respectively, but did not affect τ for $[Cu(dpp)_2^+]^*$ [22]. The use of Eq. 1 allowed the calculation of k_q values for the individual pressures from which were determined the $\Delta V^{\ddagger}_q$'s -5.4 and -6.2 cm^3 mol^{-1} for the quenching of $[Cu(dmp)_2^+]^*$ by methanol and acetonitrile, respectively. Although the partial molar volumes of *neither* the excited state $[Cu(dmp)_2^+]^*$ *nor* of the putative excited state/Lewis base complex are known, one may safely conclude that forming the latter should lead to reduced total partial molar volume. Thus, an associative pathway, such as illustrated in Scheme I, where $k_q = K_b k_n'$ should display a negative $\Delta V^{\ddagger}_q$. The negative values both of $\Delta V^{\ddagger}_n$ and of $\Delta V^{\ddagger}_q$ for $[Cu(dmp)_2^+]^*$ are consistent with the major role of associative pathways for the deactivation of this MLCT ES. Correspondingly, the medium insensitive lifetime for $[Cu(dpp)_2^+]^*$ with but a small negative value of $\Delta V^{\ddagger}_n$ confirms the role of the bulky 2,9-diphenylphenanthroline ligand in blocking access of various bases to metal coordination sites of the MLCT excited state

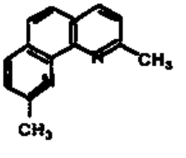
Figure 1: Dependence of MLCT lifetimes of $Cu(dmp)_2^+$ and of $Cu(dpp)_2^+$ in CH_2Cl_2 on pressure at 23 °C.



dpp =

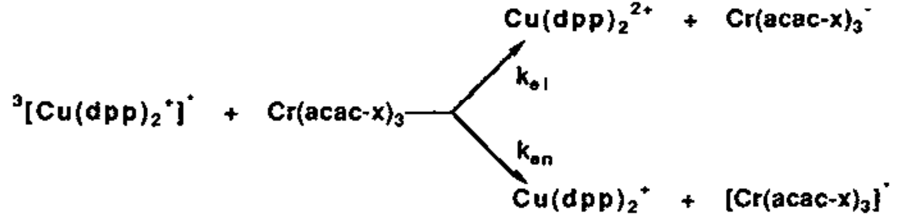


dmp =



Energy and Electron Transfer Quenching of [Cu(dpp)$_2^+$]*

That the MLCT ES of the Cu(dpp)$_2^+$ ion *is* susceptible to quenching by various electron and energy acceptors has been demonstrated [23] for a series of electron and energy acceptors such as the β-dionato derivatives CrL$_3$ (Eq. 5). These Cr(III) complexes display a remarkable range of reduction potentials (-0.79 V to -2.43 V referenced to ferrocenium/ferrocene in CH$_2$Cl$_2$ dependent on the nature of L) [23], but their doublet ligand field ES energies are relatively invariant (12.5 ± 0.4 x 10^3 cm^{-1}) [24]. These uncharged complexes are an attractive series of quenchers given the absence of ground state (GS) ion pairing interactions with ^{3}[Cu(dpp)$_2^+$]*. Electron transfer leads to charge creation, i.e., formation of a dication Cu(dpp)$_2^{2+}$ and of anions CrL$_3^-$, but energy transfer does not. Rates of electron transfer should thus be the more susceptible to perturbations of the medium.

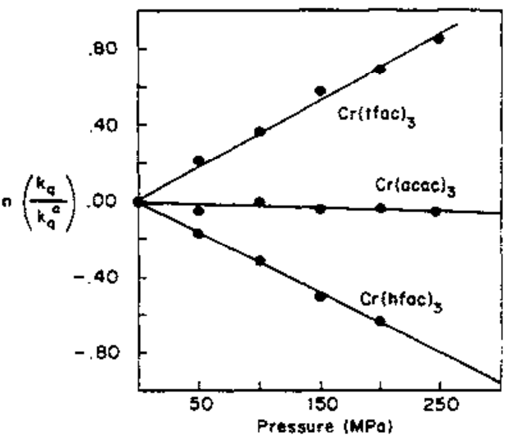


(5)

Table 2 lists the k$_q$ and ΔV$^‡_q$ values determined for quenching of ^{3}[Cu(dpp)$_2^+$]* by different CrL$_3$ complexes plus *p*-dinitrobenzene and *p*-chloronitrobenzene, the low reduction potentials and high triplet state energies of which limit their quenching of ^{3}[Cu(dpp)$_2^+$]* to electron transfer pathways [25]. Figure 2 displays ΔV$^‡_q$ plots for Q = Cr(acac)$_3$, Cr(tfac)$_3$ and Cr(hfac)$_3$, and illustrates three markedly different responses of k$_q$ to pressure, the respective ΔV$^‡_q$ values being -0.1 ± 0.8, -8.1 ± 1.0 and +8.0 ± 0.8 cm^3 mol^{-1}.

The three pressure effects illustrated by Figure 2 represent three different regimes of the ΔG°$_{el}$ for electron transfer. For those CrL$_3$ such as

Figure 2: Plots of ln(k$_q$/k$_q^a$) vs P for quenching of ^{3}[Cu(dpp)$_2^+$]* by Cr(tfac)$_3$ (upper), Cr(acac)$_3$ (middle) and Cr(hfac)$_3$ (lower) in dichloromethane at 23 °C.



$Cr(acac)_3$ where ΔG^o_{el} is unfavorable, the quenching process is dominated by the relatively slow energy transfer mechanism. In this regime, $\Delta V^{\ddagger}_q$ is quite small, consistent with the absence of solvation/desolvation effects from charge creation, and probably indicating that neither $^3[Cu(dpp)_2{}^+]^*$ nor the doublet ES formed by energy transfer to CrL_3 are dramatically distorted from the respective ground state configurations. (This result also suggests that the $\Delta\overline{V}$ for formation of the precursor complex for electron transfer would be small as well [25].) At the other extreme is the case where ΔG^o_{el} is large and negative, and k_q approaches the diffusion limit (10^{10} $M^{-1}s^{-1}$). In this regime, $\Delta V^{\ddagger}_q$ is large and positive (+8.0 ± 0.8 cm^3 mol^{-1} for $Cr(hfac)_3$) and reflects the increased viscosity and consequential decreased diffusion rates in solution. The third regime, appears where the value of ΔG^o_{el} falls slightly to the positive side of zero. When this is the case, the dominant pressure sensitive term in the absence of ion pairing must be the rate of electron transfer within the precursor complex. As would be expected for the increased solvation and

Table 2 k_q's at ambient pressure and $\Delta V^{\ddagger}_q$'s for quenching of emission from $^3[Cu(dpp)_2{}^+]^*$ in dichloromethane.

Q	$E_{1/2}{}^a$	$\Delta G_{el}{}^b$	$k_q(10^7\ M^{-1}s^{-1})$	$\Delta V_q{}^{\ddagger}(cm^3mol^{-1})$
$Cr(hfac)_3$ ^{c}	-0.79	-0.62	940	+8.0
p-dinitrobenzene -	1.18	-0.23	1050	+6.9
$Cr(tfbzac)_3$	-1.43	-0.02	200	+0.8
$Cr(tta)_3$	-1.43	0.02	220	+2.1
$Cr(tc\text{-}bzac)_3$	(-1.48)	(0.07)	60	+3.8
$Cr(br\text{-}dbm)_3$	(-1.53)	(0.12)	4.2	-3.5
$Cr(n\text{-}acac)_3$	(-1.57)	(0.16)	6.3	-3.8
p-chloronitrobenzene	-1.58	0.17	3.0	-20.4
$Cr(tfac)_3$	-1.64	0.23	4.2	-8.1
$Cr(tc\text{-}acac)_3$	(-1.66)	(0.25)	3.4	-1.4
$Cr(br\text{-}acac)_3$	(-1.89)	(0.48)	6.7	-2.4
$Cr(dbm)_3$	-1.87	0.46	6.8	-0.3
$Cr(acac)_3$	-2.43	1.02	1.5	-0.1

a $E_{1/2}$ values versus the $Fe(cp)_2{}^+/Fe(cp)_2$ couple in CH_2Cl_2 [23]; values in parentheses estimated from parameters according to reference [26].

b $\Delta G_{el}{}^o = -\{E_{1/2}(Cr^{III}/Cr^{II}) - E_{1/2}(Cu^{II}/{}^*Cu^{I})\}$

c acac = acetylacetone; dbm = dibenzoylmethane ; hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; tfbzac = 4,4,4-trifluorobenzoylacetone; tta = thenoyltrifluoroacetone; tc-bzac = 2-thiocyanato-1-phenyl-1,3-butanedione; br-dbm = 2-bromo-1,3-diphenyl-1,3-propanedione; tfac = 1,1,1-trifluoro-2,4-pentanedione; n-acac = 3-nitro-2,4-pentanedione; tc-acac = 3-thiocyanato-2,4-pentanedione; br-acac = 3-bromo-2,4-pentanedione solvent rearrangement from the resulting charge creation, a large and negative value of $\Delta V^{\ddagger}_{q}$ might be expected. Two of the quenchers in Table 2 provide dramatic examples of this effect, Cr(tfac)$_3$ ($\Delta G^{o}_{el} = 0.23$ V, $\Delta V^{\ddagger}_{q}$ -8.1 ± 1.0 cm^3 mol^{-1}) and *p*-chloronitrobenzene ($\Delta G^{o}_{el} = 0.17$ V, $\Delta V^{\ddagger}_{q}$ -20 ± 5 cm^3 mol^{-1}). This behavior suggests that under these conditions the electron transfer is closely coupled to solvent relaxation processes.

The above summary illustrates the effects of hydrostatic pressure on the rates of bimolecular excited state quenching. While the pressure experiment clearly is not sufficient to delineate the mechanism of such a process, it does add new mechanistic insight which is complementary to other, more commonly used, investigative methods applied to excited state chemistry.

Acknowledgments: This research was supported by National Science Foundation grants to PCF (CHE87-22561 and CHE90-24845).

REFERENCES

1 P. C. Ford, Chapt. 6 in "Inorganic High Pressure Chemistry, Kinetics and Mechanisms", R. van Eldik (ed.), Elsevier: Amsterdam, **1986**; p. 295.
2 H. G. Drickamer, *Ann. Rev. Phys. Chem.* **1982**, *33*, 25.
3 R. van Eldik, T. Asano, W. J. le Noble, *Chem. Rev.* **1989**, *89*, 549.
4 J. DiBenedetto, P.C. Ford, *Coord. Chem. Rev.*, **1985**, *64*, 361 and references therein.
5 J. DiBenedetto, V. Arkle, H. Goodwin, P. C. Ford, *Inorg. Chem.* **1985**, *24*, 455.
6 W. Weber and P.C. Ford, *Inorg. Chem.* **1986**, *25*, 1088.
7 S. Wieland, J. DiBenedetto, R. van Eldik, P.C. Ford, *Inorg. Chem.* **1986**, *25*, 4893.
8 M. Fetteroff, A. E. Friedman, Y. Y. Yang, H. Offen, P. C. Ford, *J. Phys. Chem.* **1988**, *92*, 3760.
9 S. Wieland, R. van Eldik, D. C. Crane, P. C. Ford, *Inorg. Chem.*, **1989**, *28*, 3663.
10 T. W. Swaddle, *Inorg. Chem.* **1990**, *29*, 5017.
11 D. Miller, P. Miller, N. A. P. Kane-McGuire, *Inorg. Chem.* **1983**, *22*, 3833.
12 P. C. Ford, *Coord. Chem. Rev.* **1982**, *44*, 61 .
13 M. E. Frink, D. Magde, D. Sexton; P. C. Ford, *Inorg. Chem.* **1984**, *23*, 1238.
14 J. DiBenedetto, Ph.D. Dissertation, U. California, Santa Barbara, **1985.**
15 N. S. Issacs, "Liquid Phase High Pressure Chemistry" J. Wiley & Sons, New York, 1981.
16 D. M. Roundhill, H. B. Gray, C.-M. Che, *Acc. Chem. Res.* **1989**, *22*, 55.
17 J. R. Peterson, K. Kalyanasundaram, *J. Phys. Chem.* **1985**, *89*, 2486.
18 D. M. Roundhill, S. Atherton, Z. Shen *J. Am. Chem. Soc.* **1987**, *109*, 6076.
19 D. R. Crane, P. C. Ford, *J. Am. Chem. Soc.* **1990**, *112*, 6871
20 E. Harvey, Ph.D. Dissertation, California Institute of Technology, 1990.
21 D. R. McMillin, J. R. Kirchhoff, K. V. Goodwin, *Coord. Chem. Rev.* **1985**, *64*, 83; *Inorg. Chem.* **1987**, *26*, 875
22 D. R. Crane, J. DiBenedetto, C. E. A. Palmer, D. R. McMillin, P. C. Ford, *Inorg. Chem.* **1988**, *27*, 3698.
23 R. Gamache, R.Rader, D. R. McMillin, *J. Am. Chem. Soc.* **1985**, *107*, 1141.
24 A. M. Fatta, R. L. Lintvedt; *Inorg. Chem.* **1971**, *10*, 478.
25 D. R. Crane; P. C. Ford, *J. Am. Chem. Soc.*, in press, 1991.
26 R. F. Handly, R. L. Lindvedt, *Inorg. Chem.* **1974** *13*, 893.