Acknowledgment. Financial support by Faculty Research Funds granted by the University of California, Santa Cruz, CA, is gratefully acknowledged.

Registry No. 1, 14837-73-1; **2**, 77403-03-3; $K_3Fe(CN)_6$, 13746-66-2.

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Received May 28, 1985

Delayed Fluorescence and Triplet-Triplet Annihilation in a Diplatinate(II) Pyrophosphite Complex

Sir:

The luminescence from salts of the tetrakis(μ-pyrophosphito)diplatinate(II) ion is of current interest.[1-8] In addition to the known fluorescence and the phosphorescence, we have observed, for the first time, anti-Stokes delayed fluorescence for crystals of the potassium salt, $K_4[Pt_2(P_2O_5H_2)_4]$, at 4.2 K. When the crystalline complex, prepared as described previously,[6] is excited by 450-nm dye laser light in its triplet state at 4.2 K, delayed fluorescence shown in Figure 1 is observed around 395 nm. The spectrum consists of a progression of the 120-cm^{-1} Pt–Pt stretching vibration, and the whole spectral distribution is exactly identical with the normal fluorescence observed at 4.2 K. Thus it is clear that the first singlet excited state (S_1) is somehow created from the first triplet excited state (T_1). At such a low temperature (4.2 K) thermal excitation from T_1 to S_1 is impossible. The most reasonable interpretation, therefore, appears to be that S_1 is created by the annihilation of two T_1's. Taking this viewpoint, we will see if the intensity and decay behaviors of the phosphorescence and the delayed fluorescence are satisfactorily interpreted in terms of this mechanism.

The kinetic equations for the populations of T_1 and S_1 are

$$dn_T/dt = -k_P n_T - k_{TT} n_T^2 \qquad (1)$$

$$dn_S/dt = -k_F n_S + f k_{TT} n_T^2 \qquad (2)$$

where k_P and k_F are respectively the first-order decay rate constants for T_1 and S_1 and k_{TT} is the rate constant for the triplet-triplet annihilation. Further, f stands for the fraction of the annihilation rate constant yielding S_1 among the total annihilation rate constant. From these rate equations we have the following expressions for n_T and n_S:

$$\frac{1}{n_T(t)} = \left(\frac{1}{n_T(0)} + \frac{k_{TT}}{k_P}\right)\exp(k_P t) - \frac{k_{TT}}{k_P} \qquad (3)$$

$$\left(\frac{1}{n_S(t)}\right)^{1/2} = \left[\left(\frac{1}{n_S(0)}\right)^{1/2} + \left(\frac{k_F k_{TT}}{f k_P^2}\right)^{1/2}\right]\exp(k_P t) - \left(\frac{k_F k_{TT}}{f k_P^2}\right)^{1/2} \qquad (4)$$

We first focus attention on the phosphorescence decay. If we plot the reciprocal of the phosphorescence intensity with respect to $\exp(k_P t)$, we would expect a straight line with a negative intercept. Such plots are attempted in Figure 2, where $1/k_P = 6.5$ ms determined from the decay obtained in a weak exciting light limit is used. The three plots correspond to three decays obtained with different exciting light intensity. All the three plots are linear and extrapolate to the same intercept. Further, the initial triplet populations obtained from the slopes and the intercept of the experimental plots are roughly in the ratio of the exciting light intensity.

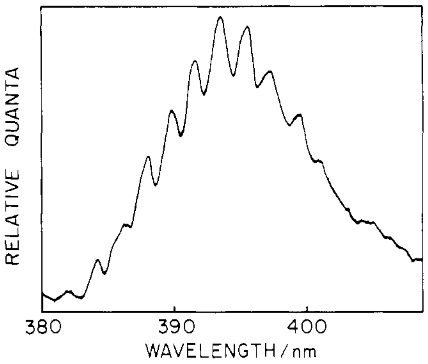

Figure 1. Delayed fluorescence spectrum of crystalline $K_4[Pt_2(P_2O_5H_2)_4]$ at 4.2 K. Excitation was by a nitrogen laser pumped dye laser (Molectron UV24 and DL14P) at 450 nm. The output from a Hamamatsu R928 photomultiplier tube was recorded with a PAR 162 boxcar integrator with 2-ms delay from the excitation and 200-μs window. The spectral distribution is exactly identical with the normal fluorescence, which is known to decay with a lifetime of less than 1 ns.

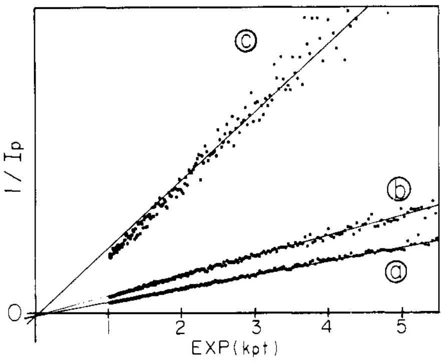

Figure 2. Plots of the reciprocal of the phosphorescence intensity with respect to $\exp(k_P t)$, where k_P is the first-order phosphorescence decay rate constant. The decay was obtained with an Iwatsu DM901 digital memory. The three plots labeled as a, b, and c correspond to three decays obtained with different exciting light intensities with a ratio of 1:0.48:0.12. In accord with eq 3, all the three plots are linear with the same negative intercept.

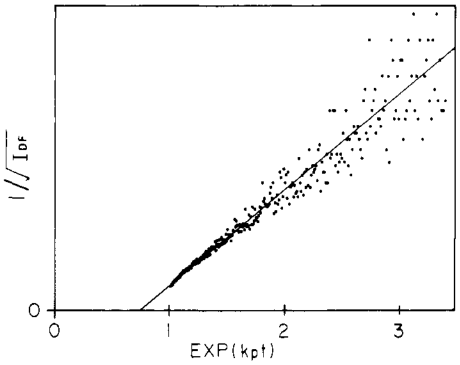

Figure 3. Plot of the reciprocal of the square root of the delayed fluorescence intensity with respect to $\exp(k_P t)$. The decay was obtained by a photon-counting system composed of a Hamamatsu C767 photon counter, C716 preamplifier, R649 photomultiplier tube, and an Ortec 6240B multichannel analyzer. In accord with eq 4, the plot is linear with a negative intercept.

We next examine the decay of the delayed fluorescence. The reciprocal of the square root of the delayed fluorescence intensity

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is plotted with respect to the same quantity as above in Figure 3. In accord with eq 4, the plot is approximately linear with a negative intercept.

In conclusion, all the features of the phosphorescence and the delayed fluorescence are satisfactorily interpreted in terms of a mechanism in which the annihilation of two triplet states yields the singlet excited state. Delayed fluorescence due to this mechanism has been observed quite extensively for organic molecules,[9] and a few examples exist for metalloporphyrins.[10] However, with regard to pure inorganic complexes, this is the first observation of delayed fluorescence. Another point to be emphasized is that the triplet–triplet annihilation investigated here is significantly more efficient than that found for organic molecules. In the majority of cases studied for organic compounds, the decay of the delayed fluorescence is nearly exponential and the lifetime is half of that of the phosphorescence. Such behavior is expected only in the low limit of the triplet–triplet annihilation. In the present case we are able to analyze the nonexponential behavior because the annihilation is so efficient. An evaluation of the annihilation rate as well as an analysis focusing attention on the triplet sublevels is in progress and will be discussed elsewhere.

Acknowledgment. We wish to thank Professors T. Nakajima and Y. Sasaki for discussions.

Registry No. $K_4[Pt_2(P_2O_5H_2)_4]$, 79716-40-8.

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Received September 17, 1985

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Articles

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π-Bond Strengths in $HP{=}PH$, $H_2P{=}P$, $HP{=}NH$, and $HN{=}NH$

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Received May 23, 1983

The chemistry of the $HP{=}PH$ π bond found in the recently isolated diphosphene compounds is considered in several ways. The $P{=}P$ π-bond strength is found by computing the rotation barrier (36 kcal/mol) and is compared to that found for $HN{=}NH$ (63.5 kcal/mol) and $HP{=}NH$ (47 kcal/mol). The structure of the HPPH anion is presented. Various electronic states of the H_2PP isomer are considered and compared to those of HPPH. Dipole moments and PP stretching frequencies are reported. The concerted hydrogenation of diphosphene is also examined.

Introduction

A major research topic in main-group inorganic chemistry in recent years has been the investigation of multiple bonding by elements in the third and higher rows of the periodic table. Because of the relative weakness of such multiple bonds most of the early work focused on multiple bonds involving only one such element. Such bonds are now commonplace. For example, the multiple bonding of silicon to such second row elements as carbon and oxygen has recently been reviewed.[1]

Molecules containing multiple bonds between two heavy atoms are much less common. Cowley[2,3] has recently reviewed the field of double bonding beteween two atoms of Si, Ge, Sn, P, or As, as well as a very few mixed double bonds between these elements.

The present work seeks to add to the body of knowledge concerning the $-P{=}P-$ linkage, found in the class of compounds named diphosphenes. One such compound, phosphobenzene, was proposed over 100 years ago,[4] but was subsequently shown by X-ray diffraction to exist in polymeric form.[5] Therefore the first report of an actual $P{=}P$ bond was the detection[6,7] in the mid-1960s by mass spectrometry of the parent diphosphene, HPPH, as an intermediate gas-phase species. The first isolable diphosphene was reported in 1981[8] and owed its existence to the bulkiness of its substituents. The numerous diphosphenes reported since then all share the same bulkiness in their ligands, which are commonly large aryl, amino, or alkyl groups. Cowley[2] has reviewed the very rich chemistry of the $P{=}P$ bond. It is reactive toward electrophiles, leading to either addition or cleavage products. It is subject to radical attack. Recently[9] the $P{=}P$ bond has also been shown to be reactive towards nucleophiles. Diphosphenes form thiiranes (containing PSP three-membered rings) and hypervalent oxides ($-(P{=}O){=}P-$) or sulfides. They also can form coordination complexes with transition metals.

The chemistry of this bond is of course dominated by the presence of its low-lying π^* orbital. Evidence for this orbital's accessibility is the red color of the diphosphenes. More quantitatively, the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitation energies[2] are about 2.6–2.9 and 3.5–3.8 eV, respectively. An additional piece of evidence is the ease of electron attachment[10] to the $P{=}P$ moiety. Finally, theoretical calculations[11] show the low energy of the π^* LUMO.

Early theoretical interest[11,12] in $HP{=}PH$ focused on the cis-trans energy difference and determination of the PP bond length. Both studies reach the same conclusions: the cis form is less stable by 3–4 kcal/mol, and without d orbitals the PP bond distance is overestimated by 0.13 Å. The interaction of N lone pairs with the $P{=}P$ bond in $N{-}P{=}P{-}N$ compounds has recently been studied.[13] NMR coupling constants for $HN{=}NH$, $HP{=}PH$,

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