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Supplementary Material Available: Tables of crystal structure data collection and refinement parameters (Table X1) and final atom positional and anisotropic temperature factors (Table X2) and Figure 3 showing the S atom labeling scheme for the ET molecule (3 pages). Ordering information is given on any current masthead page.

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(18) L.M.S. and P.T.C. are student undergraduate participants sponsored by the Argonne Division of Educational Programs from Grinnell College, Grinnell, IO, and Carthage College, Kenosha, WI, respectively.

(19) F.B. is on leave from the University of Wisconsin, Kenosha, WI.

(20) Laboratory graduate student participant sponsored by the Argonne Division of Educational Programs from Purdue University, West Lafayette, IN.

Chemistry and Materials Science and
Technology Divisions
Argonne National Laboratory
Argonne, Illinois 60439

Jack M. Williams*
Hau H. Wang
Mark A. Beno
Thomas J. Emge
L. M. Sowa[18]
P. T. Copps[18]
F. Behroozi[19]
L. N. Hall[20]
K. Douglas Carlson
G. W. Crabtree

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Temperature Dependence of the Quantum Yields for the Photoanation of Ru(bpy)$_2$L$_2^{2+}$ Complexes

Sir:

Recently, we reported[1] a correlation between the quantum yield for the photoanation of Ru(bpy)$_2$L$_2^{2+}$ complexes and the energy of the low-temperature emission. The observed linear correlation appeared to be consistent with the excited-state model proposed by Watts and co-workers[2] for Ru(bpy)$_3^{2+}$. We interpreted the variations in quantum yields in terms of changes in the energy difference between the emitting charge-transfer state and a thermally populated d–d state. It was clear at that time that an alternative explanation for the quantum yield dependence might lie in an activation process following population of the d–d state. In order to test this hypothesis, we embarked on a series of experiments designed to measure the temperature dependence of the photoanation process. The results of these experiments indicate that the excited-state description previously proposed[1,3] for Ru(bpy)$_2$L$_2^{2+}$ complexes is inadequate in its treatment of photosubstitution.

The quantum yields for the photoanation reactions

$$\mathrm{Ru(bpy)_2L_2^{2+} + Cl^- \rightarrow Ru(bpy)_2LCl^+ + L}$$

where L is pyridine or acetonitrile, over the temperature range of −20 to +33 °C, are illustrated in Figure 1. The temperature dependence of the quantum yield for the photoanation of Ru(bpy)$_3^{2+}$ has been included for comparison. The variations in the quantum yield for photoanation of Ru(bpy)$_2$(py)$_2^{2+}$ and Ru(bpy)$_2$(CH$_3$CN)$_2^{2+}$ are small but at the present time appear to be slightly larger than the expected experimental error. For discussion purposes we have calculated an Arrhenius activation energy of 700 cm^{-1} for the photoanation of Ru(bpy)$_2$(py)$_2^{2+}$ and Ru(bpy)$_2$(CH$_3$CN)$_2^{2+}$. In view of the difficulty of the determination, this value should be viewed only as an order of magnitude measurement. The experimental procedures as well as the data analysis have been described in a previous publication.[1] Similar determinations have been carried out with Ru(bpy)$_2$(3-iodopyridine)$_2^{2+}$ and Ru(bpy)$_2$(4-acetylpyridine)$_2^{2+}$, and comparable activation energies have been observed.

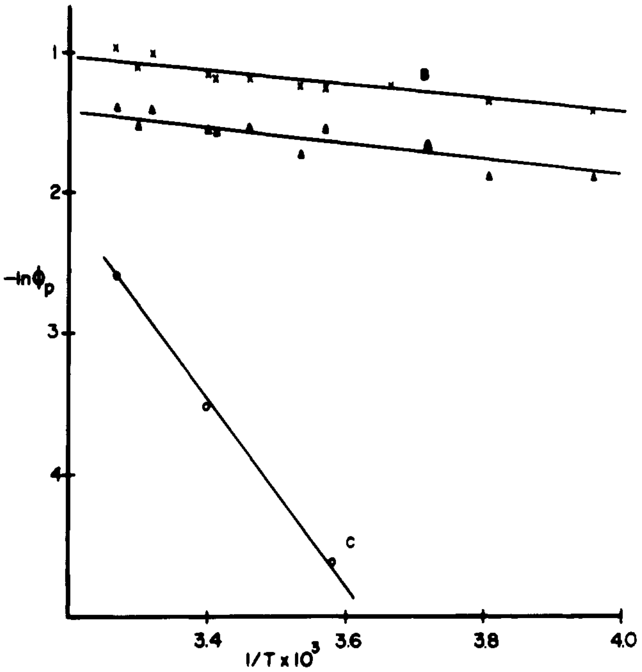

Figure 1. Temperature dependence of the quantum yields for photoanation of (A) Ru(bpy)$_2$(py)$_2^{2+}$, (B) Ru(bpy)$_2$(CH$_3$CN)$_2^{2+}$, and (C) Ru(bpy)$_3^{2+}$ in dichloromethane in the presence of excess tetrabutylammonium chloride.

The very low activation energies observed with Ru(bpy)$_2$(py)$_2^{2+}$ and the other closely related complexes indicate that the excited-state description suggested by Watts and co-workers for Ru(bpy)$_3^{2+}$ does not apply to the photoanation of complexes of the type *cis*-Ru(bpy)$_2$L$_2^{2+}$. A consideration of some results recently reported by Caspar and Meyer[3] makes this observation especially surprising. These investigations examined the luminescence lifetimes of a series of *cis*-Ru(bpy)$_2$L$_2^{2+}$ complexes as a function of temperature. The results indicated that the excited-state description of Ru(bpy)$_3^{2+}$ provided a very good model for the luminescence lifetime data obtained with a variety of Ru(bpy)$_2$L$_2^{2+}$ complexes. We have carried out similar measurements on the complexes used in this study and have observed variations in luminescence lifetimes as a function of temperature that are consistent with those observed by Meyer and co-workers. The characteristic temperature dependencies of these compounds are illustrated in Figure 2 and sharply contrast that displayed by the quantum yields for photoanation.

The different temperature dependencies exhibited by the luminescence lifetimes and the photoanation quantum efficiencies clearly indicate that photosubstitution in ruthenium complexes containing only two bipyridine ligands is not a result of thermal population of the d–d state indicated in the previous excited-state description. A d–d state is probably involved,[4] but either it must be different from the one involved in the luminescence decay or, if it is indeed the same state, it must be populated by a different pathway.

The validity of extending these results to Ru(bpy)$_3^{2+}$ is difficult to assess. In the case of Ru(bpy)$_3^{2+}$, the quantum

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(1) Pinnick, D. V.; Durham, B. *Inorg. Chem.* **1984**, *23*, 1440.

(2) Van Houten, J.; Watts, R. J. *Inorg. Chem.* **1978**, *17*, 3381.

(3) Caspar, J. V.; Meyer, T. J. *Inorg. Chem.* **1983**, *22*, 2444.

(4) Ford, P. C. *Coord. Chem. Rev.* **1982**, *44*, 61.

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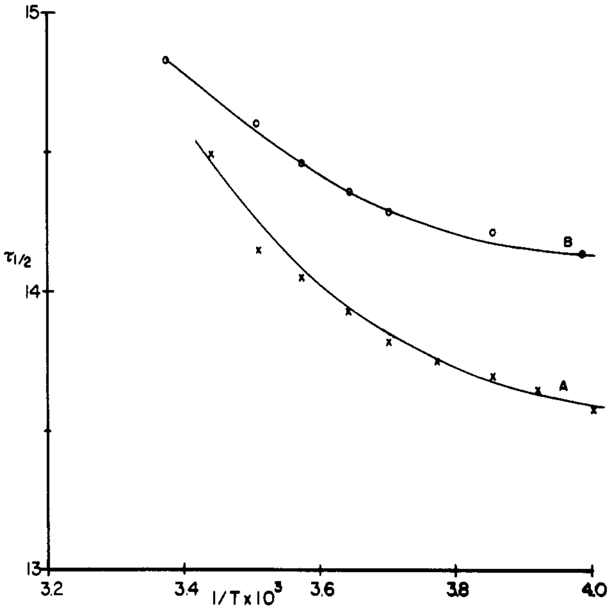

Figure 2. Temperature dependence of the luminescence lifetime of (A) $Ru(bpy)_2(py)_2^{2+}$ and (B) $Ru(bpy)_2(CH_3CN)_2^{2+}$ in dichloromethane.

yield for photoanation is strongly temperature dependent[5] but the reaction is complicated by additional temperature-dependent reactions involving competitive ring closure and chelate loss. There are currently no measurements of the efficiency of the initial ring-opening reaction. In addition to the fact that the overall photosubstitution process of $Ru(bpy)_3^{2+}$ is more complex, the effective symmetry of the disubstituted complexes may be such that the photoactive state in these complexes is inherently lower in energy than in the triply chelated complex. Interestingly, the assignment of the state that is responsible for the temperature dependence of the emission lifetime in $Ru(bpy)_3^{2+}$ as d–d was based primarily on the suppostion that photosubstitution is a consequence of populating that state.[2]

At present, there is little direct evidence to support alternative reaction paths for photoanation. We are, however, currently exploring the possibility of direct population of a d–d state from the initially populated charge-transfer state. Direct population of the d–d state would, in this case, be competitive with population of the emitting CT state. This idea is consistent with the small value and the relative ordering of the emission efficiencies of $Ru(bpy)_2(py)_2^{2+}$ and $Ru(bpy)_2(CH_3CN)_2^{2+}$. In the latter case, 30% of the absorbed photons results in photochemical reactions and is thus not available for emission. In keeping with this trend, the complex $Ru(bpy)_2(imidazole)_2^{2+}$ exhibits luminescence at room temperature comparable in intensity to that of $Ru(bpy)_3^{2+}$ and has a very low quantum yield for photoanation.

Registry No. $Ru(bpy)_2(py)_2^{2+}$, 63338-38-5; $Ru(bpy)_2(CH_3CN)_2^{2+}$, 55124-53-3; $Ru(bpy)_3^{2+}$, 15158-62-0; tetrabutylammonium chloride, 1112-67-0.

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(5) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 4803.

Department of Chemistry
University of Arkansas
Fayetteville, Arkansas 72701

David V. Pinnick
Bill Durham*

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Layered Compounds with Alternating Organic and Inorganic Layers: Vanadyl Organophosphonates

Sir:

Layered solids consisting of alternating inorganic and organic layers[1-8] are interesting because of their sorptive and catalytic properties. Compounds of this type fall into three main classes. Members of the most common class contain macroanionic inorganic layers of metal oxide or sulfide alternating with layers of charge-balancing organic cations. Examples include clays exchanged with organoammonium cations[2] and amine intercalation compounds of the layered transition-metal oxides and dichalcogenides.[3,4] In the second class, organic ligands are coordinated to transition-metal ions located within the inorganic layers, for example, $NiL_2Ni(CN)_4$,[5] $MoO_3(C_5H_5N)$,[6] and $VOPO_4(C_5H_5N)$.[7] In the third class of compound, organic groups are attached to inorganic layers by covalent bonds. Primary examples are zirconium organophosphonates and organophosphates, $Zr(RPO_3)_2$ and $Zr(ROPO_3)_2$, in which a variety of organic groups (R) are attached to the zirconium phosphate layers by covalent P–C or P–O–C bonds.[8] Compounds of the first two classes are commonly formed by intercalation of the organic groups between the preformed layers of the inorganic host, while compounds of the third class are usually crystallized directly from solutions of ionic precursors.

In recent work, the structure and topochemistry of vanadium hydrogen phosphate, $VO(HPO_4)\cdot 0.5H_2O$, have been elucidated.[9] The structure is composed of layers with hydrogen phosphate OH groups directed into the interlayer space, reminiscent of the structure of zirconium hydrogen phosphate.[10] This structural similarity has led us to attempt the synthesis of vanadium organophosphonates, which would be

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(1) Whittingham, M. S.; Jacobson, A. J. "Intercalation Chemistry"; Academic Press: New York, 1982. Dines, M. B.; Marrocco, M. In "Extended Linear Chain Compounds"; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 2, pp 1-57.

(2) Barrer, R. M. "Zeolites and Clay Minerals as Sorbents and Molecular Sieves"; Academic Press: New York, 1978; pp 407-486. Thomas, J. M.; Adams, J. M.; Tennakoon, D. T. B. *Adv. Chem. Ser.* **1977**, *No. 163*, 298-315.

(3) Schöllhorn, R.; Klein Reesink, F.; Reimold, R. *J. Chem. Soc., Chem. Commun.* **1979**, *398*. Schöllhorn, R.; Kuhlman, R.; Besenhard, J. O. *Mater. Res. Bull.* **1976**, *11*, 83-90. Schöllhorn, R.; Schulte-Nolle, T.; Steinhoff, G. *J. Less-Common Met.* **1980**, *71*, 71-78.

(4) Schöllhorn, R.; Butz, T.; Lerf, A. *Mater. Res. Bull.* **1979**, *14*, 369-376. Gamble, F. R.; Geballe, T. H. *Treatise Solid State Chem.* **1976**, *3*, 89-166. Subba Rao, G. V.; Shafer, M. W. In "Intercalated Layered Materials"; Levy, F., Ed.; D. Reidel Publishing Co.: Dordrecht, 1979, pp 99-199.

(5) Walker, G. F.; Hawthorne, D. G. *Trans. Faraday Soc.* **1967**, *63*, 166-174. Akyuz, S.; Dempster, A. B.; Morehouse, R. L.; Suzuki, S. *J. Mol. Struct.* **1973**, *17*, 105-125. Aragon de la Cruz, F.; Alonso, S. M. *Naturwissenschaften* **1975**, *62*, 298. Mathey, Y.; Mazieres, C. *J. Phys. Lett.* **1975**, *36*, L243-L245. Mathey, Y.; Mazieres, C.; Setton, R. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 1-3. Iwamoto, T. *J. Mol. Struct.* **1981**, *75*, 51-65.

(6) Johnson, J. W.; Jacobson, A. J.; Rich, S. M.; Brody, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 5246-5247. Johnson, J. W.; Jacobson, A. J.; Rich, S. M.; Brody, J. F. *Rev. Chim. Miner.* **1982**, *19*, 420-431.

(7) Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Rich, S. M. *Inorg. Chem.* **1982**, *21*, 3820-3825.

(8) Mikulski, C. M.; Karayannis, N. M.; Minkiewicz, J. V.; Pytlewski, L. L.; Labes, M. M. *Inorg. Chim. Acta* **1969**, *3*, 523-526. Yamanaka, S. *Inorg. Chem.* **1976**, *15*, 2811-2817. Alberti, G; Constantino, U.; Alluli, S.; Tomassini, J. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1113-1117. Dines, M. B.; DiGiacomo, P. *Inorg. Chem.* **1981**, *20*, 92-97. Dines, M. B.; Griffith, P. C. *Inorg. Chem.* **1983**, *22*, 567-569. Dines, M. B.; Cooksey, R. E.; Griffith, P. C.; Lane, R. H. *Inorg. Chem.* **1983**, *22*, 1003-1004. Dines, M. B.; Griffith, P. C. *Polyhedron* **1983**, *2*, 607-611. Casciola, M.; Constantino, U.; Fazzini, S.; Tosoratti, G. *Solid State Ionics* **1983**, *8*, 27-34.

(9) Johnson, J. W.; Johnston, D. C.; Jacobson, A. J.; Brody, J. F. *J. Am. Chem. Soc.*, in press. Leonowicz, M. E.; Johnson, J. W.; Brody, J. F.; Shannon, H. F.; Newsam, J. M. *J. Solid State Chem.*, in press. Bordes, E.; Courtine, P.; Johnson, J. W. *J. Solid State Chem.* **1984**, *55*, 270-279. Torardi, C. C.; Calabrese, J. C. *Inorg. Chem.* **1984**, *23*, 1308-1310.

(10) Clearfield, A.; Smith, G. D. *Inorg. Chem.* **1969**, *8*, 431-436.

0020-1669/84/1323-3842$01.50/0