Kinetic analysis of Scheme I leads to $1/\Phi = 1/a + k_d/[ak_r(\mathrm{K})]$ in the absence of quencher where a is the quantum yield of fluorenone triplets. Extrapolation of the straight-line portion of Figure 1 shows $a = 0.93$, which is in excellent agreement with the previously determined value.[10]

In the presence of quencher $\Phi_0/\Phi = 1 + k_q(\mathrm{Q})/[k_d + k_r(\mathrm{K})]$. Assuming for di-*t*-butyl nitroxide a k_q of 2×10^9 l. mole^{-1} sec^{-1}, and using the slope terms from Figures 1 and 2, provides $k_d = 1.5 \times 10^6$ sec^{-1} and $k_r = 2.7 \times 10^8$ l. mole^{-1} sec^{-1}. This value for k_r for the triplet fluorenone–**4** reaction is very close to that derived for the triplet benzophenone–**4** reaction (4×10^8 l. mole^{-1} sec^{-1}).[1b]

We believe the striking decrease in the quantum yield for adduct formation at higher ketenimine concentrations is due to deactivation of the fluorenone singlet state *via* complex formation with ground-state **4** as shown in Scheme II. The extent of complexation relative to emission (6) or intersystem crossing (7) increases with an increase in ketenimine concentration.

Scheme II

$$^1\mathrm{F}^* \xrightarrow{k_e} \mathrm{F} + h\nu \qquad (6)$$

$$^1\mathrm{F}^* \xrightarrow{k_x} {}^3\mathrm{F}^* \qquad (7)$$

$$^1\mathrm{F}^* + \mathrm{K} \xrightarrow{k_c} {}^1\mathrm{F}^*,\mathrm{K} \longrightarrow \mathrm{F} + \mathrm{K} \qquad (8)$$

Such a scheme would predict fluorescence quenching as well as a decrease in intersystem crossing efficiency at higher concentrations of **4**. Indeed, semiquantitative emission studies at room temperature show quenching of the fluorenone fluorescence in the presence of **4**.[11] There is no observable wavelength shift in the fluorenone emission in the presence of **4**,[12] nor is there any evidence for ground-state complexation from absorption spectra measurements. Classical singlet–singlet energy transfer cannot account for this quenching because of the unfavorable disposition of the energy levels in the potential donor and acceptor.

Others have reported similar observations. Hammond and co-workers report the fluorescence quenching of aromatic hydrocarbons by conjugated dienes[13] and Leonhardt and Weller describe the fluoresence quenching of perylene by amines.[14] Both groups similarly ascribe this phenomenon to complexation.

The absence of singlet quenching in the benzophenone–**4** reaction[1b] may simply be related to a shorter lifetime for the singlet state of benzophenone.[15] Studies are in progress to elucidate better the mechanism and generality of this type of quenching in organic photochemical reactions.

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[10] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 131.

[11] We thank Professor N. C. Yang for use of his emission spectrometer.

[12] At 0.2 *M* **4** the fluorenone emission is 89% quenched, and at 0.006 *M* **4** it is *ca.* 5% quenched.

[13] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966).

[14] H. Leonhardt and A. Weller in "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962, p 74.

[15] The lifetime of the benzophenone singlet has been estimated at $<2 \times 10^{-10}$ sec (W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961)), while the lifetime of singlet fluorenone was recently estimated at $<10^{-7}$ sec.[8]

Complexes Containing the $[\mathrm{Nb_6Cl_{12}}]^{3+}$ and $[\mathrm{Nb_6Cl_{12}}]^{4+}$ Cluster Ions[1]

Sir:

Previous studies have shown that $[\mathrm{Nb_6Cl_{12}}]^{2+}$ undergoes a two-electron oxidation when titrated with iodine or oxidized polarographically.[2] However, no solid compounds of the oxidized niobium cluster ion were isolated. In the case of the related $[\mathrm{Ta_6Cl_{12}}]$ cluster, oxidation states of 2+, 3+, and 4+ have been found in aqueous solutions,[2,3] and solid derivatives of the 4+ ion have been isolated.[2] We now report the preparation and properties of some complexes containing the $[\mathrm{Nb_6Cl_{12}}]$ unit in both the 3+ and 4+ oxidation states.[4] Recently it was learned that results similar to those reported here also have been obtained by Schneider and Mackay at Stony Brook, N. Y.[5] Since the derivatives prepared and, to some extent, the results obtained are somewhat different from those of Schneider and Mackay, we are prompted to this preliminary report of our results.

The preparation of these new complexes involves the dissolution of $\mathrm{Nb_6Cl_{14} \cdot 8H_2O}$[6] in methanol or ethanol, with subsequent oxidation and crystallization. The hydrated $\mathrm{Nb_6Cl_{14}}$ is used as a starting material rather than anhydrous $\mathrm{Nb_6Cl_{14}}$ because the latter dissolves very slowly.

Preparation of $[(\mathrm{C_2H_5})_4]_x\mathrm{Nb_6Cl_{18}}$ (x = 2, 3). For the 4+ compound (x = 2) 1.5 g of $\mathrm{Nb_6Cl_{14} \cdot 8H_2O}$ was dissolved in about 200 ml of absolute ethanol. The dark green (essentially black) solution was saturated with anhydrous hydrogen chloride, oxidized with chlorine gas, and then flushed with nitrogen to remove excess chlorine. Tetraethylammonium chloride (1.12 g, 2.5 mole excess) in ethanol was added, and the dark red-brown solution was resaturated with hydrogen chloride and warmed on the hot plate for 2 hr. At this point the crystallization which had begun as soon as the tetraethylammonium chloride had been added was nearly complete. The jet black needles (1.7 g) were

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; Contribution No. 1920.

[2] R. E. McCarley, B. G. Hughes, F. A. Cotton, and R. Zimmerman, *Inorg. Chem.*, **4**, 1491 (1965).

[3] J. H. Espenson and R. E. McCarley, *J. Am. Chem. Soc.*, **88**, 1063 (1966).

[4] These were first reported in a more general discussion of the chemistry of the $[\mathrm{Nb_6X_{12}}]$ and $[\mathrm{Ta_6X_{12}}]$ cluster species presented before the symposium "The Metal–Metal Bond in Inorganic Chemistry," at the 151st Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[5] R. F. Schneider and R. A. Mackay, State University of New York, Stony Brook, N. Y., private communication. We are grateful to these authors for a preliminary report of their results.

[6] New methods for the preparation of $\mathrm{Nb_6X_{14}}$ and $\mathrm{Nb_6X_{14} \cdot 8H_2O}$ (X = Cl, Br) are to be published. In the course of the preparative studies in this laboratory, some questions regarding the composition of various hydrate preparations have arisen. It appears as if the hydroxide group has been substituted into some of the chloride positions. Further investigation of this problem will be carried out. For a discussion of some aspects of hydroxide substitution, see R. J. Allen and J. C. Sheldon, *Australian J. Chem.*, **18**, 277 (1965).

Table I

Compound	Solid color	λ_{max}, mμ^a	μ, BM
$](C_2H_5)_4N]_2Nb_6Cl_{18}$	Black	~925, 454, 298, 234	0.02^b
$[(C_2H_5)_4N]_3Nb_6Cl_{18}$	Dark brown	~970, 435, 289, 218	1.65^b
$[(C_6H_5)_4As]_2Nb_6Cl_{16}(OH)(H_2O)$	Brown	~970, 430, 288	1.46^b
$[(C_6H_5)_4As]_3Nb_6Cl_{17}(OH)$	Dark brown	~970, 434, 291	Paramagnetic
$[(C_6H_5)_4As]_2Nb_6Cl_{17}(H_2O)$	Dark brown	~975, 431, 290	Paramagnetic
$Nb_6Cl_{14} \cdot 8H_2O$	Black	914, 401, 278	Diamagnetic

^{a} Spectra obtained in methanol. All solutions were prepared and maintained at room temperature. ^{b} Moment obtained from Curie law plot; measured from 77 to 300°K.

collected on a frit, washed with ethanol, and dried *in vacuo*. *Anal.* Calcd for $[(C_2H_5)_4N]_2Nb_6Cl_{18}$: Nb, 38.28; Cl, 43.83, C, 13.20; H, 2.77. Found: Nb, 38.44; Cl, 43.52; C, 13.73; H, 2.81.

The preparation of the 3+ complex ($x = 3$) was completely analogous except that air oxidation was utilized, rather than oxidation by chlorine. The product was microcrystalline and dark brown but appeared red-brown under the microscope. *Anal.* Calcd for $[(C_2H_5)_4N]_3Nb_6Cl_{18}$: Nb, 35.14; Cl, 40.23; C, 18.17; H, 3.81. Found: Nb, 35.47; Cl, 40.08; C, 18.48; H, 4.14.

Preparation of $[(C_6H_5)_4As]_2Nb_6Cl_{16}(OH)(H_2O)$. $Nb_6Cl_{14} \cdot 8H_2O$ (1 g) was dissolved in 80 ml of methanol with heating, and then 8 ml of concentrated aqueous hydrochloric acid was added. Tetraphenylarsonium chloride (2.10 g) in 15 ml of methanol was then added, and the solution was heated at the boiling point where, as oxidation proceeded, it slowly changed color from dark green to red-brown. Oxygen was bubbled through the solution for 1 hr prior to cooling and crystallization. The brown crystals (1.4 g) were collected on a frit, washed with methanol, and air dried. *Anal.* Calcd for $[(C_6H_5)_4As]_2Nb_6Cl_{16}(OH)(H_2O)$: Nb, 28.92; Cl, 29.43; C, 29.91; H, 2.30; O, 1.66. Found: Nb, 28.99; Cl, 29.23; C, 29.22; H, 2.45; O, 1.46 (determined by neutron activation analysis.)

The preparations of $[(C_6H_5)_4As]_3Nb_6Cl_{17}(OH)$ and $[(C_6H_5)_4As]_2Nb_6Cl_{17}(H_2O)$ were analogous to the above except that progressively higher concentrations of hydrogen chloride were maintained in the solution before crystallization of the product. *Anal.* Calcd for $[(C_6H_5)_4As]_3Nb_6Cl_{17}(OH)$: Nb, 23.95; Cl, 25.90; C, 37.16; H, 2.64; O, 0.69. Found: Nb, 24.11; Cl, 26.34; C, 37.44; H, 2.79; O, 0.91. Calcd for $[(C_6H_5)_4As]_2Nb_6Cl_{17}(H_2O)$: Nb, 28.66; Cl, 30.99; C, 29.64; H, 2.18. Found: Nb, 28.53; Cl, 30.50; C, 29.78; H, 2.61.

All of the complexes prepared are slightly soluble in acetone and methanol and less soluble in ethanol. They are insoluble in water and apparently inert to air. A summary of some data obtained on these compounds is presented in Table I.

It is evident that in preparing the complexes in a solvent saturated with hydrogen chloride that a terminal chloride has been coordinated to each niobium atom in the Nb_6Cl_{12} cluster. The structure might be expected to contain a regular octahedron of niobium atoms with bridging chlorides in the normal positions,[7] and with six other chlorides bonded to the apices of the octahedron. In this arrangement no intercluster bonding is allowed and the isolated ions, $[(Nb_6Cl_{12})Cl_6]^{n-}$, are obtained.

In the preparations of the tetraphenylarsonium complexes a much lower concentration of chloride ion was used, and also air oxidation[8] was relied on to oxidize the cluster unit. The evidence for hydroxide or water being bonded to the cluster is, in addition to the analytical data, the visible spectra and magnetic moments which indicate a 3+ oxidation state for the cluster. We have been unable to unambigously assign any bands in the infrared spectra which may arise from coordinated water or hydroxide in these tetraphenylarsonium salts.

It appears that the number of aquo or hydroxyl groups which are coordinated to the $[Nb_6Cl_{12}]^{3+}$ unit is determined by the relative hydrogen chloride concentration in the solution. At the lowest hydrogen chloride concentration, $[(Nb_6Cl_{12})Cl_4(OH)(H_2O)]^{2-}$ was obtained, whereas in ethanol saturated with hydrogen chloride $[(Nb_6Cl_{12})Cl_6]^{3-}$ was obtained.

At this time the spectral data are incomplete, and it has not been established to what extent the ions of the type $Nb_6Cl_{12}Cl_6^{n-}$ may undergo replacement of chloride by solvent molecules. However, the spectra show the interesting trend that the two principal bands in the visible and near-ultraviolet region are shifted to lower energies by about 1500 cm^{-1} on each increase in the oxidation state of the cluster. The intensities of these bands undergo little change. The band in the 950-mμ region is not shifted so regularly and shows some significant intensity variation. The position of the band in the 400–450-mμ region has served as a useful diagnosis of the oxidation state of the cluster.

The magnetic studies have yielded the result that the 2+ and 4+ cluster derivatives are diagmagnetic, whereas the 3+ derivatives are paramagnetic. The small moment (0.02 BM) obtained for the 4+ derivative listed in Table I is attributed to about 1% 3+ impurity.

A detailed and systematic study on the preparation, spectra, and magnetic susceptibilities of $[M_6X_{12}]^{n+}$ complexes is currently in progress.

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(7) A. Simon, H. G. Schnering, H. Wöhrle, and H. Shäfer, *Z. Anorg. Allgem. Chem.*, **339**, 155 (1965).

(8) It has been observed that prolonged exposure to air of solutions saturated with hydrogen chloride leads to deposition of mixtures containing the cluster in both the 3+ and 4+ oxidation states.

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Cyclopropyl Semidiones[1]

Sir:

The question of delocalization in cyclopropylcarbinyl systems has been investigated by a study of semidiones

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(1) Aliphatic Semidonies. IV. This work was supported by a grant from the National Science Foundation.