any specific yield resulting from direct excitation; furthermore, we would definitely expect that use of different kinds of sensitizers (*e.g.*, neutral aromatic, cationic, etc.) would necessarily result in different sensitized quantum yields. We therefore conclude that, while the study of excited state quenching by energy or electron transfer may be intrinsically interesting, and while study of energy transfer processes may aid in the resolution of some of the problems of ligand field photochemistry, there is no clear way to relate intermolecular energy transfer studies to intrinsic processes within "molecular" charge transfer states of coordination complexes.

References and Notes

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Synthesis and Structure of Dinuclear Niobium and Tantalum Complexes Containing an Unusual Bridging Ligand Derived from Acetonitrile

Sir:

In earlier work in this laboratory[1] it was found that the tantalum(IV) halides, $TaCl_4$ and $TaBr_4$, undergo unexpectedly complicated reactions when dissolved in acetonitrile. These reactions provided a red, soluble fraction containing 80–100% of the tantalum as unidentified products. In addition an insoluble fraction containing 0–20% of the tantalum was obtained as a green crystalline powder. Although the composition of the green products was somewhat variable, it always was close to that expected for the tantalum(III) adducts $TaX_3(CH_3CN)_3$, X = Cl or Br.

Subsequent work showed that these green compounds were diamagnetic, did not reduce Fe(III) when treated with aqueous iron(III) sulfate, and hydrolyzed instantly in water to produce tantalum(V) oxide. Such behavior was inconsistent with that expected for compounds containing tantalum in a reduced oxidation state.[2] By contrast the niobium(IV) halides NbX_4 (X = Cl, Br, I) react under the same conditions to provide the simple adducts $NbX_4(NCCH_3)_2$.[3]

In the unusual reactions leading to the green products some evidence indicated that Ta(III) might play an intermediate role, as in the scheme

$$2\mathrm{Ta(IV)} \longrightarrow [\mathrm{Ta(III)}] + \mathrm{Ta(V)}$$

$$[\mathrm{Ta(III)}] + \mathrm{CH_3CN} \longrightarrow \text{green products}$$

As predicted from this scheme, addition of zinc to the initial TaX_4-acetonitrile mixtures at room temperature afforded much improved yields of the green products (20–50% of the initial tantalum). Similarly analogous products were obtained when solutions of $NbCl_4$ in acetonitrile were reduced with zinc.

In a typical reaction 5.0 g (0.021 mol) of $NbCl_4$ and 0.69 g (0.011 mol) of granular zinc were treated with 30–50 ml of acetonitrile in an evacuated flask with stirring for 4–7 days. After removing acetonitrile by vacuum distillation, the powdered mixture was transferred to the fritted glass filter of an extractor adapted for high vacuum work and subsequently extracted with dry acetonitrile until the red soluble material was completely removed. The less soluble green powder then was dried under high vacuum and analyzed. *Anal.* Calcd for $NbCl_3(CH_3CN)_3$: Nb, 28.83; Cl, 33.00; C, 22.34; H, 2.82; N, 13.03. Found: Nb, 28.86; Cl, 32.74; C, 23.97; H, 3.44; N, 11.95. The corresponding product from the reaction of $TaCl_4$ and acetonitrile was obtained in exactly the same way. *Anal.* Calcd for $TaCl_3(CH_3CN)_3$: Ta, 44.10; Cl, 25.92; C, 17.56; H, 2.21; N, 10.24. Found: Ta, 44.36; Cl, 26.51; C, 17.99; H, 2.55; N, 9.96.

The infrared spectra of these products indicate that both acetonitrile and a new ligand (L) derived from acetonitrile are coordinated to the metal. In acetonitrile, reaction of these compounds with LiCl or bis(triphenylphosphine)iminium chloride, $[(C_6H_5)_3P]_2N^+Cl^-$, leads to substitution of 1 mol of CH_3CN/mole of metal, and with CsCl to 2 mol of CH_3CN/mole of metal. (As shown below, the structure of the $[(C_6H_5)_3P]_2N^+$ salt containing niobium has been determined, and, taken together with the infrared spectra, the data indicate all of the compounds are correctly formulated as dimers.) Thus the substitution reactions provide salts containing the anions $[M_2Cl_8(NCCH_3)_2L]^{2-}$ and $[M_2Cl_{10}L]^{4-}$, where L = $C_4H_6N_2$. A comparison of the infrared spectra of $[M_2Cl_6(NCCH_3)_4L]$ with those of $Cs_4[M_2Cl_{10}L]$ clearly reveal the bands of *L* at 2920–2930 (w), 2850–2860 (w), 1430–1433 (w), 1370–1382 (m),

Table I. Bond Distances (Å) and Angles (deg) in the Anion $[Nb_2Cl_8(CH_3CN)_2(C_4H_6N_2)]^{2-}$

Nb–Cl(1)	2.410 (2)	N(L1)–C(N1)	1.378 (8)
Na–Cl(2)	2.408 (2)	N(L2)–C(N2)	1.144 (8)
Nb–Cl(3)	2.425 (2)	C(N1)–C′(N1)	1.35 (1)
Nb–Cl(4)	2.399 (2)	C(N1)–C(M1)	1.48 (1)
Nb–N(L1)	1.752 (6)	C(N2)–C(M2)	1.47 (1)
Nb–N(L2)	2.411 (6)		
N(L2)–Nb–N(L1)	176.9 (3)	C′(N1)–C(N1)–C(M1)	120.9 (9)
Nb–N(L1)–C(N1)	178.1 (6)	N(L2)–C(N2)–C(M2)	178.9 (10)
N(L1)–C(N1)–C(M1)	114.4 (9)	Nb–N(L2)–C(N2)	172.5 (7)
N(L1)–C(N1)–C′(N1)	124.7 (9)		

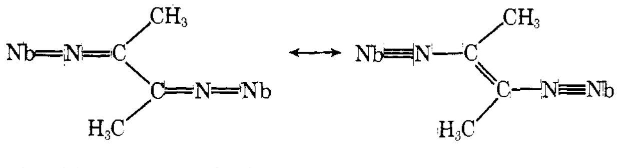
1348-1366 (s), 1097-1103 (m), 1019-1025 (w), 919-929 (w), and 652-662 (s) cm^{-1}.

Crystalline material suitable for X-ray diffraction work was obtained with the $[(C_6H_5)_3P]_2N^+$ salt of the $[Nb_2Cl_8(NCCH_3)_2L]^{2-}$ anion. A mixture containing $[(C_6H_5)_3P]_2N^+Cl^-$ and $[Nb_2Cl_6(NCCH_3)_4L]$ in a 2:1 mole ratio was dissolved in 30 ml of acetonitrile to provide a green solution. After addition of 60 ml of chlorobenzene chunky green crystals were deposited. These were filtered under nitrogen, washed with chlorobenzene, and dried *in vacuo*. A suitable crystal was selected, mounted in a sealed Lindeman capillary, and subjected to X-ray structure determination.

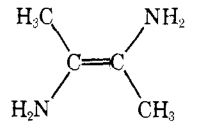
The monoclinic space group was determined to be $P2_1/n$, with the unit cell parameters a = 14.95 (1) Å, b = 20.96 (1) Å, c = 15.09 (1) Å, and β = 105.9 (1)°. The structure was determined using 4754 reflections with intensities $I \geq 3\sigma(I)$ out of the 7300 measured, and phased by the heavy atom procedure. After several electron density syntheses, all 57 nonhydrogen atoms in the asymmetric unit were located; subsequent full-matrix least-squares refinements and electron density difference syntheses revealed the locations of 40 of the 41 hydrogen atoms in the asymmetric unit. Further anisotropic refinement converged to a final R value (defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.066. The successful refinement of the structure determined the previously unknown composition as $\{[(C_6H_5)_3P]_2N\}_2[Nb_2Cl_8(CH_3CN)_2(C_4H_6N_2)]\cdot 2C_6H_5Cl$, and for the unit cell Z = 2, V = 4547.09 Å^3, and d(calcd) = 1.414 g cm^{-3}, with only one-half the formula unit per asymmetric unit.

The essential feature of the structure concerning the anion is depicted by the computer-generated drawing shown in Figure 1. Of special interest is the bridging $CH_3CNCNCH_3$ ligand derived from the reductive coupling of two acetonitrile molecules. In the anion there is an inversion center at the midpoint between C(N1) and C′(N1); thus, the four atoms in the bridging chain N(L1)-C(N1)-C′(N1)-N′(L1) are rigorously required by symmetry to lie in the same plane. The two niobium atoms are only slightly displaced from this plane (0.01 Å), and the two C atoms of the methyl groups similarly are displaced by only 0.03 Å. Some key bond distances and angles within the anion are listed in Table I.

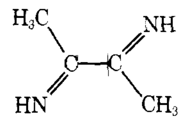
Bond distances worthy of special comment are Nb-N(L1) (1.752 (6) Å), which is indicative of double or triple bond character,[4] N(L1)-C(N1) (1.378 (8) Å), which is intermediate between those expected for a single or double bond, and C(N1)-C′(N1) (1.35 (1) Å), which is near that expected for olefins. Since the bond angle Nb-N(L1)-C(N1) is very nearly 180°, the lone pair density on N(L1) must be small. These data strongly suggest that the π bonding is extensively delocalized over the metal atoms and bridging ligand chain, as indicated by the resonance



At this point insufficient evidence has been obtained to determine if the bridging ligand is better regarded as the tetraanion of the *trans*-diaminoolefin (1) or the dianion of the diimine (2). However, the coplanarity of the C-N skeleton, trans configuration, and bond distances are possibly more supportive of the tetraanion of **1**.



1



2

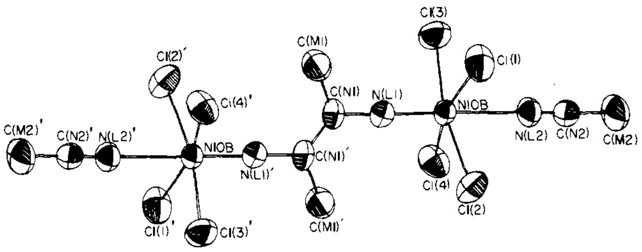


Figure 1. Structure and labeling scheme of the anion $[Nb_2Cl_8(CH_3CN)_2C_4H_6N_2]^{2-}$.

The relation is uncertain between the $[Ta_2Cl_6(NCCH_3)_4(C_4H_6N_2)]$ reported here and the compound prepared by Blight, *et al.*,[5] by reaction of $TaCl_4$ with acetonitrile. The latter was reported as a metal-metal bonded dimeric complex of Ta(III), $Ta_2Cl_6(NCCH_3)_4$.[5] It seems likely that the compounds are actually identical although in the latter case no mention was made of the characteristic bands of the bridging ligand $C_4H_6N_2$ in the inrared spectra. More recently, Gert and Perron[3] noticed that a green compound formulated as $TaCl_3(NCCH_3)_3$ was formed when $TaCl_5$ was reduced with Sn, Zn, or Al in acetonitrile. Work done in this laboratory subsequently has shown that reduction of $TaCl_5$ with zinc, as reported by Gert and Perron, provides the same compound reported here as $[Ta_2Cl_6(NCCH_3)_4(C_4H_6N_2)]$. Further work on the properties, mode of formation, and reactions of compounds containing these interesting bridging ligands is in progress.

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Identification of Tryptophan Resonances in Natural Abundance Carbon-13 Nuclear Magnetic Resonance Spectra of Proteins. Application of Partially Relaxed Fourier Transform Spectroscopy

Sir:

In recent years, numerous ^{13}C nmr studies of proteins have been reported.[1-8] Some of the reports have covered general features in the natural abundance ^{13}C nmr spectra of aqueous proteins in various states.[1,4] Others have dealt with ^{13}C nmr signals of incorporated ^{13}C-enriched amino