analysis of six reactions, each of which included a set of eight alkyl groups.[18] They used the expression log $k = \alpha + \beta_1\theta_1 + \beta_2\theta_2$, analagous in form to the Taft equation, and evaluated six α, six β_1, six β_2, eight θ_1, and eight θ_2 values. The θ_1 terms are correlated strongly with E_s, while θ_1 and θ_2 are themselves uncorrelated. The nonsteric term $\beta_2\theta_2$ is claimed to be statistically significant.

Closer examination of the data set shows serious deficiencies which invalidate the entire study. For example, reaction 1 is stated to be base-catalyzed hydrolysis of amides, but comparison of rate constants recalculated from the reported β_1 and β_2 values with the literature shows that the data are instead for an alternative set of acid-catalyzed hydrolysis of amides[19,20] and that reaction 1 therefore duplicates reation 6. Reaction 5, pK_a values for RCOOH, shows too narrow a range to provide useful discrimination.

Without these two reaction sets there are too few data to provide a reliable statistical evaluation of the total set of α's, β's, and θ's. But there are yet further problems with the data set. Comparison with other reaction series shows that some of the rate constants for R = *t*-Bu are outliers. The rate constants reported for acid-catalyzed hydrolysis of *t*-BuCONH$_2$ are too high by a factor of more than 3 (reactions 1 and 6)[13,19,20] while the rate constant reported for base-catalyzed hydrolysis of *t*-BuCOOEt in 85% ethanol is too low by a factor of 2.[13,17] The statistical significance of the $\beta_2\theta_2$ term is therefore an artifact of these numerous faults in the data set. In statistical terminology the data set analyzed does not properly represent the intended population.

If the purpose of an investigation is to measure steric effects of alkyl groups or of alicyclic structures, there will by little error in assuming that polar effects are constant among all substituents for any reaction having ρ_1 less than about 15. This includes acid-catalyzed and base-catalyzed acyl-transfer reactions (esterification, hydrolysis, ester exchange, etc.) and a wide rate of other reaction types. The way is now open for greatly expanding the experimental evaluation of steric effects.

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(21) **Note Added in Proof.** Communication with Drs. M. Sjöström and S. Wold indicates that the data for reaction 1 of ref 18 came from ref 22. Curiously the rate constants for alkaline hydrolysis of RCONH$_2$[22] are nearly identical with the reworked rate constants for sulfuric acid catalysis.[19] In fact, α_1, β_{11}, and β_{12} correlate either set equally well;[18] the Bruylants' data for alkaline hydrolysis are similar but are not as well correlated by these constants. Reexamination of the Bolton data substantiates his claim that amide hydrolyses do not follow the Taft equation very well. If we use the data at 75 °C for the RCH$_2$CONH$_2$ set[19] to define a (=1.1157) and ρ_s (=1.0465) of eq 2, with $\rho_1 = 0$, giving a standard deviation of 0.06 in log k(calcd), then the observed rates for the several R$_1$R$_2$COHCONH$_2$ examples are too fast on average by a factor of 1.8 and *t*-BuCONH$_2$ is too fast by a factor of 7. The full matrix statistical treatment[18] is a relatively crude technique since it is sensitive to random errors and outliers. Based on extensive data[13] we would expect ester reactions to follow the Taft equation closely with $\rho_1 = 0$. Since the θ_1 values[18] correlate with E_s, we would thus expect the $\beta_2\theta_2$ terms to be indistinguishable from zero for ester reactions 2, 3, and 4[18] while the $\beta_2\theta_2$ term would be significant for the amide reactions 1 and 6. This prediction holds for all reactions except for reaction 4,[18] alkaline hydrolysis in 85% ethanol; this set includes a *t*-Bu outlier value. For the related hydrolysis in 70% acetone[16] where the *t*-Bu value is normal, $\beta_2 = 0.17 \pm 0.18$, indistinguishable from zero. The causes of the difference in behavior of amides and esters are not obvious and the situation deserves further exploration.

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Received July 17, 1980

Triangular Triniobium Cluster in Aqueous Solution

Sir:

Recent work on molybdenum and tungsten species in aqueous solutions has revealed the existence of trinuclear, triangular metal clusters in oxidation states between 3+ and 5+.[1-10] The aim of the present work is to explore the possibility that similar triangular clusters may occur in species of other transition elements of the second and third row in aqueous solution.

We report here the first of such species, a triangular niobium cluster prepared by reduction of Nb(V) in aqueous solution.

The aqueous chemistry of niobium in oxidation states lower than 5+ has not been characterized due to the lack of definite structural information.[11] Although the reduction of Nb(V) in mineral acids was used in both qualitative and quantitative determination of this element, the nature of the reduced species remained unknown.[12] One of these species, a red-brown anion, obtained by reduction of pentavalent niobium in aqueous H$_2$SO$_4$, has been the subject of many studies in this century.[14] Most investigators assigned hexanuclear structures to this species.[14e-g] We now report the results of an X-ray structure analysis[15] of the potassium salt of this species, which was prepared as described previously.[14e] The correct formula derived from the structure is $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$. The molecular scheme is shown in Figure 1. It reveals that this much investigated compound is, in fact, a trinuclear, triangular niobium cluster and that previously proposed structures were erroneous.

The overall geometry of the complex is reminiscent of a structural and coordination type found in compounds with the general formula $[M_3X_2(O_2CR)_6L_3]^{n(\pm)}$ (M = Mo, W; X = O, CCH$_3$; L = H$_2$O, OCOCH$_3$),[1,3,7] which is depicted schematically in Figure 2. The niobium cluster possesses the same kind of M$_3$O$_2$ core as in $[W_3O_2(O_2CR)_6(H_2O)_3]^{2+}$[3] but differs from diaquahydrogen these structures by its six bridging sulfates which replace the six acetates. Such bridging sulfates have not been observed before in metal clusters. With two molecules in the cell of space group $P2_1$, there is no crystallographic symmetry imposed upon the complex, but the deviations from an ideal D_{3h} symmetry are small. All the average distances between each of the niobium

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(1) (a) Bino, A.; Ardon, M.; Maor, I.; Kaftory, M.; Dori, Z. *J. Am. Chem. Soc.* **1976**, *98*, 7093. (b) Reexamination of the crystal described in ref 1a has shown that the correct formula is $[Mo_3(CCH_3)_2(OAc)_6(H_2O)_3](CF_3SO_3)_2$ with μ_3-alkylidyne capping ligands rather than the EtO$^-$ groups suggested previously. The right structure was refined in the rhombohedral system.[7]

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(11) The only exception being the well-known water soluble lower halides of the type $Nb_6X_{12}^{n+}$.[13]

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(15) The red-brown compound crystallizes in space group $P2_1$ with a = 9.961 (2), b = 18.088 (3), c = 10.036 (2) Å, β = 118.84 (2)°, and Z = 2; 2900 unique reflections with $I > 3\sigma(I)$ were used in the structure solution and refinement. The structure was solved by direct methods. Least-squares refinement converged to a discrepancy of 0.040. A detailed report will be published later. A table of atomic positional and thermal parameters is available as supplementary material.

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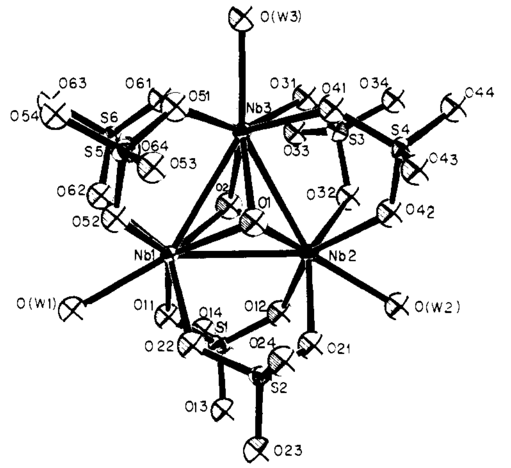

Figure 1. The structure of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$.

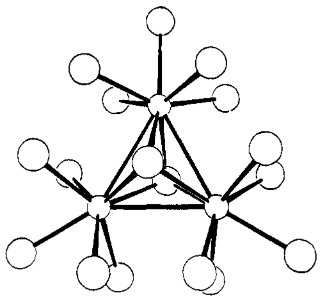

Figure 2. The skeletal structure of compounds with the general formula $[M_3X_2(O_2CR)_6L_3]^{n(\pm)}$.

Table I. Some Average Bond Distances (Angstroms) in $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$

Nb-Nb	2.886 (1)
Nb-(μ_3-O)	2.052 (9)
Nb-O(μ-SO_4)	2.136 (9)
Nb-O(H_2O)	2.241 (9)
O···H···O($H_5O_2^+$)	2.42 (1)

atoms and its seven surrounding oxygen atoms are similar to those found in the Mo and W complexes. Some pertinent bond distances are given in Table I.

The $H_5O_2^+$ ion occurs in this structure with an O···H···O distance of 2.42 (1) Å. This result is within the average range of 2.41–2.45 Å found in other compounds containing the diaquahydrogen ion.[16] The visible spectra of the niobium cluster in the solid state, in the mother liquid, and in a solution prepared by dissolving the solid in 60% H_2SO_4 were compared and found to be identical.[17] This, together with the fact that the red-brown solid is precipitated quantitatively from the red-brown solution by adding K_2SO_4, strongly supports the assumption that the species present in the solution is identical with the ion found in the crystal, namely, $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$. The 5– charge of the niobium cluster necessitates a nonintegral oxidation number of $3^2/_3+$ for the metal atoms. This result agrees with the results of Golibersuch and Young, who determined the oxidation state of the niobium atom in this complex by a permangantometric titration.[14e] These results suggest that there are four electrons involved in the Nb–Nb bonding. According to Cotton's MO calculations for metal clusters,[18] these four electrons occupy bonding orbitals and the resulting bond order in this complex is $^2/_3$. The same bond order was assigned to the structurally related triangular molybdenum cluster $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^{2+}$;[1] the oxidation state of the molybdenum atoms is $4^2/_3+$ and four electrons are involved in the Mo–Mo bonding. The metal-metal bond length is 2.887 (1) Å, in good agreement with the Nb–Nb bond length reported here, 2.886 (1) Å, for the same bond order.

Supplementary Material Available: Positional and thermal parameters for the atoms of $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$ (2 pages). Ordering information is given on any current masthead page.

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[17] Both solid (KBr pellet) and solution show absorption lines at 510 and 700 nm. The solution spectrum is in agreement with that reported earlier by Goroshchenko and Andreeva which was, however, wrongly assigned to a postulated $Nb_6O_3(SO_4)_8$.[14g]

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Received July 31, 1980

Isolation and Structure of Spatol, a Potent Inhibitor of Cell Replication from the Brown Seaweed *Spatoglossum schmittii*

Sir:

Cytotoxicity is a frequently encountered pharmacological property associated with extracts of marine organisms,[1] and in several cases the cytotoxic agents have been purified and described.[2] The utilization of these cytotoxins in the selective inhibition of cancer cell replication represents a long-term goal of marine cytotoxicity investigations. To promote this application, we have adopted a convenient field-oriented bioassay involving the assessment of inhibition of the synchronous cell division of the fertilized sea urchin egg. Preliminary pharmacological studies have indicated that the urchin egg assay may be highly selective for compounds which inhibit mitotic spindle formation via inhibition of tubulin polymerization.[3] This mechanism of action

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