

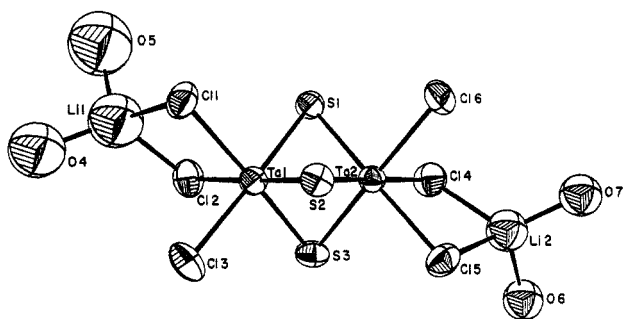


Figure 1. ORTEP drawing of the $[\text{Ta}_2\text{Cl}_6(\text{THT})_3][\text{Li}(\text{THF})_2]$ molecule. Carbon atoms of the THF and THT rings have been omitted for the sake of clarity. Thermal ellipsoids enclose 40% of electron density. Ta, S, and Cl atoms were refined anisotropically. Important, averaged interatomic dimensions: Ta(1)–Ta(2), 2.626 (1) Å; Ta–S, 2.392 [4] Å; Ta–Cl, 2.494 [3] Å; Ta–Cl(Li), 2.525 [6] Å; Li–Cl, 2.42 [2] Å; Li–O, 1.96 [5] Å; Ta–S–Ta, 66.3 [2]°; S–Ta–S, 92.7 [4]°.

quite surprising, viz., $[\text{Li}(\text{THF})_2]_2[\text{Ta}_2(\mu\text{-THT})_3\text{Cl}_6]$, it was a Ta(II) dimer with a short metal–metal distance (vide infra).¹¹ The original synthetic procedure was reproducible, but since it was too elaborate and not very efficient, a superior method was subsequently developed. It involves reduction of $\text{Ta}_2\text{Cl}_6(\text{THT})_3$ in THF with 2 equiv of sodium amalgam in the presence of LiCl. The product is isolated in high yield (>60%) after filtration and addition of hexane. The proton NMR spectrum¹² in acetonitrile- d_3 indicates that the complex is diamagnetic and all three THT ligands are equivalent. The tetrabutylammonium derivative was also prepared, by cation exchange, and its crystallographic characterization carried out.¹³

The molecular structure determinations of both the lithium and tetra-*n*-butylammonium salts revealed discrete confacial bioctahedra with a $\text{Ta}_2(\mu\text{-S})_3\text{Cl}_6$ frame. An ORTEP drawing of the former is shown in Figure 1 and important interatomic dimensions are listed in the figure caption. The most notable feature of the dinuclear anion is the short Ta–Ta distance of about 2.62 Å. It is distinctly shorter than the double bonds in species of the type $\text{M}_2\text{X}_6\text{L}_3$ and $\text{M}_2\text{X}_6\text{L}_4$, M = Nb and Ta, with bridging atoms from the third period (the typical distance is around 2.7 Å, and the shortest observed is equal 2.6695 (5) Å). This together with the $d^3\text{--}d^3$ electronic configuration and diamagnetism of the compound indicates the presence of a formal triple Ta–Ta bond. A more detailed description of metal–metal bonding is difficult because the presence of three bridging atoms usually complicates the

interpretation of the interactions between central atoms in confacial bioctahedra.¹⁴ In addition, since analogous compounds with other transition metals are apparently unknown the discussion of metal–metal interactions based upon comparison of relevant interatomic dimensions presents problems as well. The nonahalo-metalates are not appropriate for the purpose as they do not exhibit a straightforward relationship between the number of d electrons and the M–M distance.¹⁴ Among the M_2X_9 species there are a few compounds with some degree of similarity to $[\text{Ta}_2(\text{THT})_3\text{Cl}_6]^{2-}$. They are $\text{Mo}_2\text{Cl}_6(\text{SMe}_2)_3$,¹⁵ which has a similar composition, and $\text{W}_2\text{Cl}_4(\text{SET})_3(\text{SMe}_2)_2$,¹⁶ which has the same $\text{M}_2(\mu\text{-S})_3$ central core. These complexes have formal metal–metal bonds order of 3 and 2.5, respectively, with the M–M bond lengths equal 2.462 (2) and 2.505 (1) Å, respectively. The difference of ca. 0.16 Å between the triple bond of Mo and Ta is not particularly abnormal. The former usually forms stronger bonds than Nb and Ta which have more diffuse d orbitals. This seems to be reflected in shorter M–Cl(terminal) distances for Mo and W but the different nature of trans ligands can also be a factor in this case.

The isolation of the Ta(II) dimer has important consequences. It provides the basis for the preparation of related Nb species and possibly compounds with unsupported triple metal–metal bonds of the type M_2X_8 . A more complete report including discussion of the electronic structure will be submitted later.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant A-494) for support.

Supplementary Material Available: Table of positional and isotropic equivalent thermal parameters for $[\text{Li}(\text{THF})_2]_2[\text{Ta}_2\text{Cl}_6(\text{THT})_3]$ (3 pages). Ordering information is given on any current masthead page.

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Concerning the Mode of Reaction of the Proposed Ultimate Metabolite of the Carcinogen 4-Nitroquinoline 1-Oxide. Evidence for Intermediacy of Nitrenium Ions[†]

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Esters of *N*-hydroxy-*N*-arylacetamides, such as **1**, are considered to be the reactive metabolites of mutagenic and carcinogenic aromatic amides.² Reaction with purines and pyrimidines in DNA has been discussed^{2,3} on the basis of a key N–O heterolysis to give an acylnitrenium ion intermediate such as **2**. However, an al-

(10) Calculations were done on the VAX-11/780 computer at the Department of Chemistry, Texas A & M University, College Station, TX, with the VAX-SPD software package.

(11) The complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.622$ (1) Å, $b = 22.468$ (3) Å, $c = 10.581$ (2) Å, $\alpha = 103.37$ (1)°, $\beta = 119.28$ (1)°, $\gamma = 85.31$ (1)°, $V = 2142$ (1) Å³, $Z = 2$, $d_{\text{calc}} = 1.779$ g/cm³ for $\text{fw} = 1141.43$. Refinement of 236 parameters using 3053 reflections with $F^2 > 3\sigma(F^2)$ produced residuals R and R_w equal to 0.062 and 0.076, respectively. The crystallographic analysis was routine without unusual problems. The apparent loss of THF during data collection (ca. 40% decay) resulted in high thermal parameters for light atoms. It did not, however, affect the refinement to a significant degree. The light Li atoms were located in the difference Fourier map and their presence is unquestionable in view of the arrangement of the THF molecules. The table of positional and isotropic equivalent thermal parameters is provided as supplementary material.

(12) The spectra were recorded on a Varian EM-390 NMR spectrometer. The proton resonances appeared as multiplets with the following chemical shifts (in ppm, vs. Me_4Si): THF 3.55 and 1.66; μ_2 -THT 3.00 and 2.06; acetonitrile 1.79; free THT (small peaks) 2.50 and 1.69.⁸ Repeated washing of the solid with hexane removed the free ligand but there was also partial loss of THF.

(13) The salt crystallizes in a noncentrosymmetric orthorhombic space group $Pc2_1a$ (No. 29) with $a = 11.646$ (3) Å, $b = 22.250$ (6) Å, $c = 22.833$ (6) Å, $Z = 4$, $V = 5913$ (3) Å³, and $d_{\text{calc}} = 1.487$ g/cm³ for $\text{fw} = 1324.06$. The intensity data set was of poor quality, apparently due to unfavorable mosaic spread. There was very little X-ray scattering above $2\theta = 30^\circ$ and all atoms, including Ta, had high thermal parameters. The whole $\text{Ta}_2\text{Cl}_6(\text{THT})_3^{2-}$ anion and most atoms in the NBu_4^+ cations were located in the difference Fourier map and refined isotropically. This allowed unequivocal identification of the compound. The interatomic dimensions within the anion compared well with those in the Li derivative.

[†] Dedicated to Professor Guy Ourisson on the occasion of his 60th birthday.

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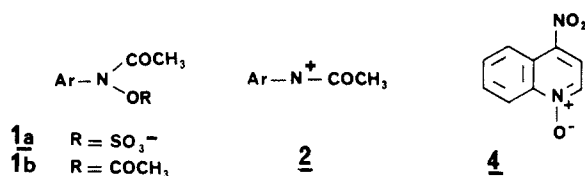
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Table I. Pseudo-First-Order Rate Constants for Solvolysis of Monoester **3**

solvent	Y_{OTs}^a	Y_{Cl}^b	k_{25}^c, s^{-1}	ρ^c
EtOH	-1.75	-2.50	2.16×10^{-4}	0.994
MeOH	-0.92	-1.20	3.50×10^{-4}	0.996
EtOH-20% H ₂ O	0	0	7.16×10^{-4}	0.998
TFE	+1.80	+2.38	4.30×10^{-3}	<i>d</i>
Me ₂ CO-H ₂ O				
90-10			2.66×10^{-4}	0.999
80-20		-0.80	5.66×10^{-4}	0.999
70-30		+0.17	8.66×10^{-4}	0.998
60-40	+0.66	+1.00	1.23×10^{-3}	0.999

^a Reference 18a. ^b Reference 18b. ^c " ρ ", correlation coefficients for a linear treatment of concentration vs. time data. ^d Rate constant extrapolated from only three plots.

ternative homolytic cleavage giving radical intermediates has also been considered.⁴ Indeed there is still little evidence of the precise pathway by which these ultimate metabolites react with DNA. Recent solvolysis studies, performed for the most part with model compounds such as sulfonate and sulfate esters^{5,6} or related carboxylate esters,⁷ show that under a variety of solvent conditions heterolysis via nitrenium ion pathways is the major pathway. For example, for cleavage of the N-O bond in a series of methane sulfonate esters of *N*-hydroxyacetanilides in chloroform ρ equals -9.24.^{5a} A complication in the study of *N*-acetoxy-*N*-arylacetyl-amides of polycyclic aromatic type is the competitive or preferential reaction by acyl-oxygen cleavage rather than by cleavage of the N-O bond.⁸ We now report a solvolytic study of the hydroxylamino acetate **3**, a compound that differs from the aforementioned series by the absence of an acyl substituent at nitrogen. Our results unambiguously establish that **3**, the proposed⁹ reactive metabolite of the powerful carcinogen 4-nitroquinoline *N*-oxide (**4**), reacts by N-O bond heterolysis. Acyl oxygen cleavage is not observed.

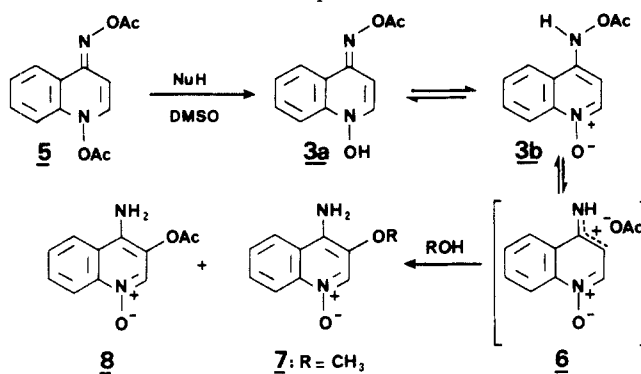


Reduction of 4NQO **4** by ascorbic acid followed by bis-esterification with acetic anhydride in acetic acid gave the crystalline ester **5**.¹⁰ Treatment of the ester **5** with a stoichiometric amount of piperidine in Me₂SO afforded only the monoester **3** by reaction at the more reactive N-1 site.^{11,12}

Solvolysis of **3** was studied (a) in a range of alcohols of varying nucleophilicity and ionizing power and (b) in a series of acetone water mixtures exhibiting a wide range of Y values. No products were observed associated with acyl-oxygen fission. Instead, typically in methanol two products **7**¹⁴ and **8**¹⁵ were formed via substitution and internal return, respectively.

Rates of solvolysis of **3** were measured to at least 90% conversion in each solvent using HPLC,¹⁶ and showed excellent pseudo-first-order kinetics (see Table I).

Although the Grunwald-Winstein relation $\log k/k_0 = mY^{17}$ seems not to have been applied to mechanistic studies of nitrenium ions, we find that in this work the rate of solvolysis correlates well with the ionizing power of the solvent (for Y_{Cl} , $\rho = 0.985$, and for Y_{OTs} , $\rho = 0.992$).¹⁸ This excellent correlation leaves little doubt that the reaction proceeds through an ionic pathway with a rate-determining step requiring charge separation in the transition state. Further the data show a lack of sensitivity of solvolysis rate to the nucleophilicity of the medium (the m value is equal to 0.26 (Y_{Cl}) and 0.36 (Y_{OTs})). In the scheme the proposed pathway requires cleavage of the N-O bond in the tautomer **3b**. Attack of a nucleophile and internal return on the delocalized nitrenium-carbenium ion **6** leads to products **7** and **8**.



A number of interesting points emerge in the comparison of these results with recent studies. First, the hydroxylamino acetate **3** behaves analogously to the hydroxamic acid esters **1** in giving products both by internal return and by substitution through N-O bond cleavage.^{5,6} However, in the case of **3** no acyl oxygen cleavage occurs. Second, solvolysis of **3** is faster by several orders of magnitude^{8c,19} than the rates found with the *N*-acetoxy-*N*-arylacetyl-amides **1b**, the postulated ultimate carcinogens of aryl-amides. This rate enhancement is attributed to a combination of two factors: a nitrenium ion from **3** is not destabilized by electron withdrawal by an acyl substituent, and a charged intermediate such as **6** will derive substantial stabilization from the

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(12) All attempts to isolate **3** from the reaction medium either by us in a number of experiments or by others¹³ have failed due to its extreme instability. However, **3** was characterized by ¹H NMR as already reported^{11,13} and the unique formation of **3** was established by HPLC. New spectral data: ¹³C NMR (Me₂SO) δ 168.85, 151.77, 138.14, 137.65, 130.69, 123.11 (two carbons), 116.51, 114.03, 91.37, 19.82; MS, 219 (MH⁺, 1%), 202 (M - O, 17%), 160 M - O - COCH₃, 42%), 144 (M - O - COCH₃, 100%), 129 (40%).

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(14) Compound **7** is a solid, yield 40% in isolated product: mp 205 °C; ¹H NMR (Me₂SO) δ 8.33 (1 H, s), 8.31 (1 H, d, $J = 9$ Hz), 8.15 (1 H, d, $J = 9$ Hz), 7.22-7.56 (2 H, m), 6.33 (2 H, s, NH₂), 3.81 (3 H, s); (M⁺) calcd 90.0742, obsd 90.0749.

(15) Compound **8** was not isolated: it decomposes during all attempted purification. However, when *t*-BuOH is used as solvolysis medium, **8** is the unique product formed, it converts spontaneously into 4-acetamido-3-hydroxyquinoline 1-oxide which could be isolated and characterized: mp 232-233 °C; ¹H NMR (Me₂SO) δ 9.70 (br s, NH and OH), 8.30-8.40 (2 H, m), 7.50-7.70 (3 H, m), 2.10 (3 H, s); IR (KBr) 3250, 3000, 1655 cm⁻¹; (M⁺) calcd 218.0691, obsd 218.0697. Yield of formation of **8** in methanol could not be rigorously determined. It is estimated to be 60% (HPLC). It corresponds to the unique peak appearing besides **7**. The dihydroxy derivative resulting from acyl-oxygen fission from **3** would have been unmistakably detected if formed as indicated by check experiments.

(16) Monoester **3** was prepared by adding 1 equiv of piperidine to diester **5** in Me₂SO. Solvolysis samples were obtained by immediate dilution with the appropriate solvent to give solutions 4×10^{-3} in **3** and 2% in Me₂SO.

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(19) Compare the value measured in Me₂CO-H₂O (60:40) for **3** at 25 °C: $k = 1.23 \times 10^{-3}$ to those reported^{8c} for a series of *N*-acetoxyacetaminoarenes which range from 1.2×10^{-6} for the less reactive *p*-tolyl to 8.8×10^{-5} for the most reactive fluorenyl system in the same solvent at 40 °C.

N-oxide functionality. This stabilization is reflected in the low *m* value indicating a low sensitivity of the stabilized nitrenium ion to the reaction medium.²⁰ Finally it has been established that both in vivo and in vitro the carcinogen 4-nitroquinoline 1-oxide **4** gives products with DNA by reaction of a nucleic base at the C-3 position of the quinoline.^{9,21} This study proves the susceptibility to nucleophilic attack of metabolites of **4** and in suggesting a nitrenium ion pathway provides a focus for further study of the interaction of carcinogens with DNA.

(20) A referee has suggested that the formation of **7** might not involve much separation of charge in the transition state but rather occur via intramolecular acetate migration or by an S_N2 process. Our conclusion that reaction is via ionization is based on the clear evidence from the Grunwald-Winstein plot of charge separation in the transition state. Our observed low *m* value we attribute to the stabilization of the *N*-oxide functionality. The comments of the referee highlight the need for further Grunwald-Winstein plots for reactions proceeding via nitrenium ion intermediates.

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EPR Study of a Cubane-Type Mixed Cluster in a Single Crystal: CoFe_3S_4 in $[\text{NBu}_4]_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$

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Mixed-metal cubane-type clusters MFe_3S_4 are of great interest because they may be good models for the active site of some metalloproteins and also for comparison of their electronic structure with that of the Fe_4S_4 parent clusters. Synthesis of compounds containing such species is a great challenge for inorganic chemistry but, up to now, only two mixed clusters have been obtained: MoFe_3S_4 and WFe_3S_4 .^{1,2} An alternative way for creating these clusters is to obtain Fe_4S_4 model compounds slightly doped with the required metal. If the mixed cluster has an odd number of electrons, it will necessarily be paramagnetic and we can hope to see an EPR spectrum associated with it if the matrix itself is diamagnetic. We report the result of such an attempt to the case of the cobalt-doped model compound $[\text{NBu}_4]_2[\text{Fe}_4\text{S}_4(\text{SPh})_4]$. An EPR spectrum clearly associated with cobalt is observed which we attribute to the heteronuclear $(\text{CoFe}_3\text{S}_4)^{2+}$ core. This study, made on single crystals, provides the first orientational information about the EPR parameters of a mixed-metal cubane-type cluster.¹²

The model compound was prepared as previously described.^{3,4} Doping with cobalt was achieved by adding 0.2% of CoCl_2 to FeCl_3 . Single crystals were grown from acetonitrile solution by a transport method. The pure compound crystallizes at room temperature in the monoclinic system.⁵ Around 240 K a phase transition occurs, the cell becoming orthorhombic below this temperature. To prevent occurrence of the phase transition the sample was quenched. At about 77 K, the quenched cobalt-doped samples do not exhibit any EPR lines but, as the temperature is decreased, composite spectra appear near $g = 2$ (see Figure 1a).

[†] Also at USTM Grenoble.

[‡] Also at CNRS.

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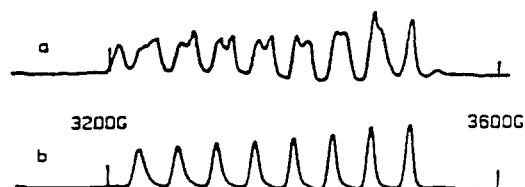


Figure 1. Second-derivative absorption EPR spectra for $\vec{H} \parallel \vec{c}^*$. Microwave frequency, 9.253 GHz; microwave power, 10 mW; 100-kHz field modulation, 2 G. (a) Two predominant $I = 7/2$ centers, including the one studied, are observed at $T \sim 10$ K. (b) Only the center studied in this work remains at $T = 4.2$ K.

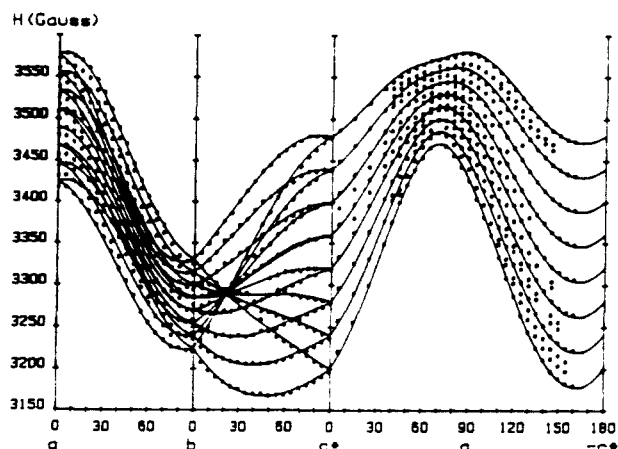


Figure 2. Experimental points and calculated angular dependences in the *ab*, *bc*^{*}, and *c*^{*}*a* planes. Mean microwave frequency, 9.165 GHz. Extra points correspond to "forbidden" lines.

Table I. Principal Values of the $\vec{g}$ and $\vec{A}$ Tensors and Their Direction Cosines in the $\vec{a}$, $\vec{b}$, $\vec{c}^*$ Frame (*A* Values in MHz)

	$\vec{a}$	$\vec{b}$	$\vec{c}^*$
$g_1 = 1.860$	0.955	0.019	0.296
$g_2 = 1.998$	0.015	0.994	-0.113
$g_3 = 1.970$	-0.296	0.112	0.949
$ A_1 = 38$	0.939	-0.108	0.328
$ A_2 = 0$	-0.017	0.935	0.355
$ A_3 = 123$	-0.345	-0.339	0.875

By varying the temperature and the microwave power four sets of lines could be distinguished, all clearly associated with cobalt ions. At 4.2 K and 10 mW of microwave power, three sets are saturated and thus only one remains. We will focus only on the latter, for which the complete angular variations could be obtained.

A typical spectrum, recorded at 4.2 K with the magnetic field $\vec{H}$ directed along $\vec{c}^*$, is shown in Figure 1b. Clearly, the eight equally spaced lines are the hyperfine components associated with the cobalt 59 nuclear spin $I = 7/2$. As the temperature is raised, the lines begin to broaden out around 15 K due to a fast spin-lattice relaxation, showing the presence of low-lying excited states. No lines indicative of an $S > 1/2$ state appear in the low-field region: we are dealing with $-1/2 \rightarrow +1/2$ transitions of an $S = 1/2$ ground state. The angular variations of the lines when $\vec{H}$ is swept in the *ab*, *bc*^{*}, and *c*^{*}*a* planes are reported in Figure 2. They show the presence of two sites which become equivalent for $\vec{H}$ along the twofold screw axis $\vec{b}$ or in the plane *c*^{*}*a*, in agreement with the monoclinic symmetry of the lattice. These angular variations are rather well fitted in a first-order perturbation approximation by the spin Hamiltonian $\vec{H}\vec{g}\vec{S} + \vec{S}\vec{A}\vec{I}$ with $S = 1/2$ and $I = 7/2$. The small discrepancies that occur between the calculated curves and the experimental points are due to second-order effects, to the nuclear quadrupole coupling neglected in the calculation, and also to some slight misalignments of the sample. The appearance of "forbidden" lines, specially in the *ab* and *c*^{*}*a* planes near the $\vec{a}$ axis, is due to this quadrupolar interaction. Table I gives the principal values of the $\vec{g}$ and $\vec{A}$ tensors and the direction cosines of their principal axes with respect to