fraction of the Np(V) ions are in a different site. The hyperfine splitting is quite large—one line at the negative extreme of the spectrum is beyond the range of the Mössbauer drive. The Mössbauer parameters of the major resonances are the magnetic hyperfine constant ($g_0\mu_N H_{\text{eff}} = 9.91 \pm 0.29$ cm/s), the quadrupole coupling constant ($^1/_4 eqQ = 2.9 \pm 0.9$ cm/s), and the isomer shift (relative to $NpAl_2$) (1.69 ± 0.21 cm/s). These values are consistent with other Np(V) compounds with magnetic hyperfine splitting at 4.2 K, such as neptunium(V) hydroxide[6] and neptunium(V) oxalate,[7] and indicate nothing unusual for the Mössbauer spectrum of the Np(V)–Cr(III) complex.

The spectrum of the Np(V)–Rh(III) complex does not correspond to any simple pattern. The resonances at −13 and +9.7 cm/s correspond to the strongest lines of magnetic hyperfine structure. From the intensity of these resonances, they represent only a minor fraction of the total neptunium. The Mössbauer parameters derived from these resonances are $g_0\mu_N H_{\text{eff}} = 9.9 \pm 0.2$ cm/s and $\delta = 1.7 \pm 0.2$ cm/s. The isomer shift value is in the proper range for a Np(V) species.

The strong resonance in the center of the spectrum of the Np(V)–Rh(III) complex represents the major fraction of the Np(V) present. This resonance is interpreted as being dominated by quadrupole splitting and is complicated by intermediate relaxation effects. In the fast relaxation limit, a spectrum collapses to a single resonance or a quadrupole-split resonance; at long relaxation times, the spectrum is magnetically split. Intermediate relaxation times produced broadened resonances,[7] and since the relaxation processes often have different rates in different directions along the lattice of a solid, an extremely strange spectrum can result. An important difference occurs between the spectra of the Np(V)–Cr(III) complex and the Np(V)–Rh(III) complex: the spectrum of the Np(V) ion in the Cr(III) complex is magnetically split; the spectrum of the Np(V) ion in the Rh(III) complex is not split.

The magnetic splitting in the Mössbauer spectrum of the Np(V)–Cr(III) complex and the lack of magnetic splitting for the major fraction of the Np(V)–Rh(III) complex are consistent with the suggested structure[3] of these complexes and the magnetic properties of the Cr(III) and Rh(III) ions. The complexes are formed by slowly replacing a water molecule in the first coordination sphere of Cr(III) or Rh(III) with the neptunyl ion NpO_2^+. The Cr(III) or Rh(III) coordinates to the Np(V) ion through one of the Np(V) oxygen atoms. Thus, the NpO_2^+ ion presumably retains its axial symmetry, but the electrostatic field on the Np(V) ion is distorted by the Cr(III) or Rh(III) ion. The field from the strongly paramagnetic Cr(III) ion ($3d^3$, high spin) induces magnetic splitting in the Mössbauer spectrum of the Np(V)–Cr(III) complex, but no splitting is induced by the diamagnetic Rh(III) ion ($4d^6$, spin = 0).

The cation-exchange resin was assumed to have little influence on the environment of the complexes or the complex ions held on the resin primarily by an ion-pair association. However, this assumption probably underestimates the possibilities that some resin sites may enter the coordination sphere of the transition metal ion or that the protons held on resin sites near the complex may influence the field on the Np(V) ion. Presumably, the magnetically split structure in the Np(V)–Rh(III) spectrum may arise through an effect of this nature.

Registry No. NpO_2^+, 21057-99-8; $Rh(H_2O)_6^{3+}$, 16920-31-3; $Cr(H_2O)_6^{3+}$, 14873-01-9.

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Conversion of Hydrous Germanium(II) Oxide to Germynyl Sesquioxide, $(HGe)_2O_3$

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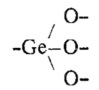
Received May 16, 1977 AIC70348S

Germanium(II) hydroxide (hydrous germanium(II) oxide) is a white, yellow, or brown noncrystalline material, only slightly soluble in water and alkaline solutions, having no definite stoichiometry, and represented by formulas such as $GeO{\cdot}xH_2O$, $Ge(OH)_2{\cdot}xH_2O$, and, loosely, $Ge(OH)_2$.[1-4] We have found that digestion of a suspension of either yellow or brown germanium(II) hydroxide in aqueous sodium hydroxide solutions yields a dark brown insoluble compound which has properties distinctly different from those of the starting hydroxide. The compound, after being thoroughly washed and dried in vacuo at room temperature, is a dark brown pyrophoric powder with a composition close to $(HGe)_2O_3$. The empirical formula and properties of the compound suggest that it is a polymer consisting of Ge–H groups linked by oxygen atoms, i.e., "germynyl sesquioxide."[5-7]

Vibrational Spectra. Infrared spectra indicate that $(HGe)_2O_3$ is structurally different from various forms of germanium(II) hydroxide which have not been treated with hydroxide solutions. Figure 1 shows the pertinent regions of Nujol and halocarbon mull spectra of germanium(II) hydroxide samples that were subjected to the various treatments outlined in Table I. The bands near 3300 and 1650 cm^{-1} which appear in some spectra (especially those of samples B and C) are undoubtedly due to water.[8] These bands were very prominent in the spectrum (not shown) of a sample which had been purposely dried less thoroughly than the other samples. Samples B and C (which had not been treated with hydroxide) showed broad absorptions in the regions of 800 and 540 cm^{-1}, in agreement with a spectrum earlier reported for $Ge(OH)_2$.[3]

The bands near 2000, 835, and 760 cm^{-1}, which appear in the spectra of the samples treated with hydroxide (D, E, and F), are characteristic of Ge–H stretching,[9] vibrations of a germanium–oxygen network of the type[7]



and Ge–H deformation,[9] respectively. It is significant that sample E (which was briefly washed with acid after the hydroxide treatment) had an infrared spectrum essentially the same as those of samples D and F. This result shows that $(HGe)_2O_3$ is not rapidly reconverted to $Ge(OH)_2$ by treatment with acid. Samples B and C, which were not treated with hydroxide, were brown and yet showed none of the distinctive absorptions characteristic of $(HGe)_2O_3$. This result shows that

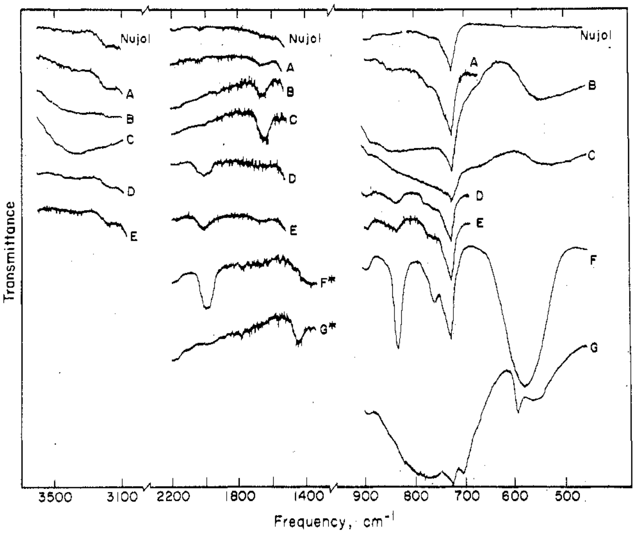


Figure 1. Infrared spectra of mulls of $Ge(OH)_2$ and $(HGe)_2O_3$. See Table I for significance of letter notations. All spectra are for Nujol mulls except F* and G*, which are for halocarbon mulls.

Table I. Physical and Chemical Treatment of Germanium(II) Hydroxide Samples Examined as Mulls by Infrared Spectrometry

Sample	Treatment[a]	Color[b]
A	Untreated[a]	Yellow
B	Digested in boiling water for 4 h	Brown
C	Boiled with 1 M H_2SO_4 for 1 h	Dark brown
D	Stirred with 7 M NaOH for 3 days at 25 °C and then washed thoroughly with water by repeated centrifugation and decantation	Brown
E	Same as D and then stirred with 1 M H_2SO_4 for 30 min and finally washed again with water as above	Brown
F	Digested in 7 M NaOH at 75 °C for 1 h and washed as above	Dark brown
G	Digested in 7 M NaOH at 75 °C for 1 h, washed thoroughly, dried in vacuo overnight, and then stirred for 1 week in D_2O	Dark brown

[a] Each sample of germanous hydroxide was precipitated and washed as described in the Experimental Section. After the indicated treatment, the sample was pumped on overnight at 0 °C. The mull was made using the resulting dried material.
[b] Color before vacuum drying. The colors darkened upon drying.

a change in the color of germanium(II) hydroxide from yellow to brown is insufficient evidence for conversion to germynyl sesquioxide.

Sample G was $(HGe)_2O_3$ which had been stirred in D_2O for 1 week. As expected, the Ge–H bonds were replaced by Ge–D bonds; hence the band at 2000 cm^{-1} was replaced by one at 1450 cm^{-1}. The spectrum of G in the low-frequency region shows new features similar to those which appear when $(HGe)_2O_3$ is stirred for long periods with H_2O. Apparently $(HGe)_2O_3$ undergoes degradation during such treatment.

A Raman spectrum of sample F showed broad bands at 2030 and 560 cm^{-1}, probably due to Ge–H and Ge–O stretching, respectively. No bands could be found in the Raman spectrum of sample A.

Pyrolysis. When ordinary germanium(II) hydroxide is heated in vacuo to 400 °C, the principal reaction is the dehydration to GeO,[10,11] although a small amount of hydrogen gas is evolved during the process.

$$Ge(OH)_2 \rightarrow GeO + H_2O$$

Table II. Pyrolysis of Germanium(II) Hydroxide and Germynyl Sesquioxide at 400 °C in Vacuo

Compd	Residue weight, g	Amt of H_2 formed, mmol	Amt of Ge, mmol	Calcd ratio H_2:Ge	Calcd ratio O:Ge in residue[a]
$Ge(OH)_2$	0.0378	<0.01	0.416	<0.02	1.1
$Ge(OH)_2$	0.1422	0.035	1.590	0.02	1.1
$(HGe)_2O_3$	0.0143	0.064	0.157	0.41	1.2
$(HGe)_2O_3$	0.0606	0.276	0.643	0.43	1.4
$(HGe)_2O_3$	0.0819	0.396	0.854	0.46	1.5

[a] Calculated assuming the residue to contain no hydrogen.

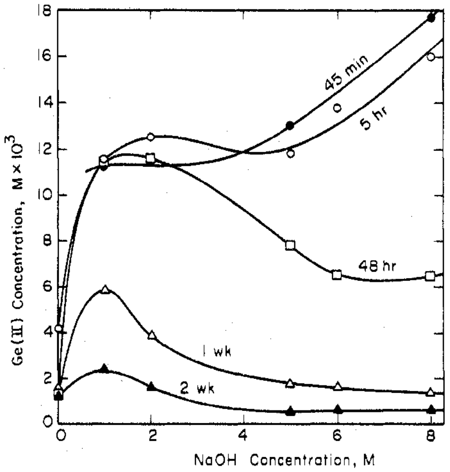


Figure 2. The solubility of $Ge(OH)_2$ as a function of time and of hydroxide concentration.

On the other hand, when germynyl sesquioxide is similarly heated, most of the hydrogen in the compound is evolved as hydrogen gas, and the residue is a mixture of GeO and GeO_2.

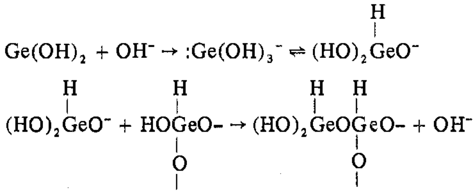
$$(HGe)_2O_3 \rightarrow H_2 + GeO + GeO_2$$

Evidence supporting these reactions is presented in Table II.

Solubility Studies. The solubility of germanium(II) hydroxide in water and in sodium hydroxide solutions has been studied by various workers.[1,2,4] The results are somewhat discordant; however, there is general agreement that the solubility is very low, i.e., <0.03 M. We believe that previous workers have not fully recognized that the nature of the solid phase changes at a measureable rate when germanium(II) hydroxide is suspended in alkaline solutions, that the rate of this change is a function of hydroxide concentration, and that consequently the measured solubility changes with hydroxide concentration and with time.

We measured the solubility of germanous hydroxide (i.e., the concentration of Ge(II) in solutions saturated with germanous hydroxide) as a function of the concentration of sodium hyroxide in the solutions and as a function of time. After initial equilibration periods of 0.5 h, the concentration of Ge(II) decreased with time—the rate of decrease being greatest in the more concentrated hydroxide solutions. The solubilities determined for several equilibration times are plotted vs. hydroxide ion concentration in Figure 2. From the curves for equilibration times of 45 min and 5 h, it can be seen that the solubility of relatively fresh $Ge(OH)_2$ increases with increasing hydroxide concentration. The measured solubilities decrease with time at all hydroxide concentrations, but especially rapidly at concentrations of 5 M and higher. The conversion of freshly precipitated, yellow, germanium(II) hydroxide to brown $(HGe)_2O_3$ is rapid (hours) in highly concentrated hydroxide solutions and slow (days) in dilute hydroxide solutions. The color of germanous hydroxide suspended in sodium hydroxide solutions appears to be closely correlated with the solubility—the dark material having a lower solubility than the light material.

These results indicate that ordinary germanium(II) hydroxide reacts with the hydroxide ion to form a soluble species, perhaps a complex such as $OGeH(OH)_2^-$. The conversion of $Ge(OH)_2$ to the relatively insoluble $(HGe)_2O_3$ appears to be catalyzed by this dissolved species or by hydroxide ions, perhaps through a mechanism such as the following.[12–15]



$$\mathrm{Ge(OH)_2 + OH^- \rightarrow :Ge(OH)_3^- \rightleftharpoons (HO)_2\overset{H}{Ge}O^-}$$

$$\mathrm{(HO)_2\overset{H}{Ge}O^- + HO\underset{O}{\overset{H}{Ge}}O- \rightarrow (HO)_2\overset{H}{Ge}O\underset{O}{\overset{H}{Ge}}O- + OH^-}$$

Experimental Section

Germanium(II) hydroxide was precipitated by the addition of aqueous ammonia to a solution of Ge(II) in hydrochloric acid.[16] This and all subsequent operations were carried out under a nitrogen atmosphere. The $Ge(OH)_2$ was collected on a sintered-glass funnel and washed with deoxygenated water. The conversion to $(HGe)_2O_3$ was effected most conveniently by stirring damp $Ge(OH)_2$ (prepared from 5 g of GeO_2) with 35 mL of 10 M NaOH at 70 °C for 1 h. The resulting dark brown solid was washed on a coarse sintered-glass funnel with deoxygenated water until the filtrate was neutral. The sample was dried to constant weight by pumping through a liquid-nitrogen trap (20 h generally sufficing). To avoid splattering of the sample, it was cooled to 0 °C during the initial pumping; yield 1.2 g (26%).

The purity of the $Ge(OH)_2$ was established by determining the equivalents of reducing power per mole of germanium. The hydrogen evolved during digestion of the material in 10 M NaOH at 120 °C for 3 days, followed by analysis for Ge by the mannitol method,[17] corresponded to 1.996 equiv/mol (theory, 2.000 equiv/mol). The $(HGe)_2O_3$ was analyzed for Ge by the mannitol titration method (after treatment with acid and peroxide). Anal. Calcd: Ge, 74.4. Found: Ge, 75.7.

Infrared spectra were obtained using mulls in Nujol or chlorofluorocarbon oil (Series 14–25, Halocarbon Products Corp., Hackensack, N.J.) between NaCl or KBr plates and a Perkin-Elmer Model 337 grating infrared spectrophotometer. Raman spectra were obtained using a Coherent Radiation Co. spectrometer (Model 1401).

Pyrolyses of damp samples of $Ge(OH)_2$ and $(HGe)_2O_3$ were carried out in a glass tube in a tube furnace. The samples were heated while continuously Toepler-pumping the evolved hydrogen through liquid nitrogen cooled traps. Germanium in the pyrolyzed residues was determined as described above. The results are presented in Table II.

All manipulations involved in the solubility measurements were carried out under nitrogen. Each $Ge(OH)_2$ slurry was stirred for a measured time; a portion of the slurry was centrifuged, and an aliquot of the clear supernatant was acidified, treated with excess standard triiodide solution, and titrated with thiosulfate.

Acknowledgment. This work was supported largely by the U.S. Energy Research and Development Administration.

Registry No. $(HGe)_2O_3$, 63937-01-9; $Ge(OH)_2$, 12024-99-6.

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X-Ray Crystal and Molecular Structure of Tetrakis(*N*,*N*-dimethyldithiocarbamato)-μ-nitrido-μ-(*N*,*N*-dimethyldithiocarbamato)-diosmium(IV)

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Received June 22, 1977 AIC70440O

There have been only a few reports of dithiocarbamato complexes of osmium.[1–4] Of these, the ones which are well characterized generally contain tertiary phosphine ligands[1,2] and in one case a tris(dithiocarbamato)osmium(III) complex has been claimed;[3] however, this compound is not well characterized. We report here the synthesis, characterization, and x-ray structure of a novel symmetric μ-nitrido-diosmium(IV) complex with the formula $Os_2N[S_2CN(CH_3)_2]_5$ where one dtc ligand also bridges the two osmium atoms. Only a few nitrido complexes of osmium are known[5–7] and none with the Os–N–Os bridge has been structurally characterized. This complex is the first well-characterized osmium–nitrido complex which contains dithio-acid ligands and it is the only example of a M–N–M complex which contains a second bridging ligand.

Experimental Section

Spectra. ^1H NMR spectra were recorded at 79.54 MHz using a Varian CFT 20 spectrometer. IR spectra were recorded in KBr disks with a Perkin-Elmer Model 237 grating spectrophotometer. Electronic absorption spectra were obtained in CH_2Cl_2 solution at 25 °C with a Cary Model 14 spectrophotometer. Magnetic susceptibilities were determined by the Faraday method at 25 °C using $Hg[Co(SCN)_4]$ as calibrant. Conductivity experiments were carried out using a Yellow Springs Instrument Co. Model 31 conductivity bridge. Reagent grade nitromethane was purified by double distillation from anhydrous $CaCl_2$ onto anhydrous $CaSO_4$ under nitrogen. Mass spectra were obtained using an AEI MS-30 mass spectrometer and samples were introduced using the solid-sample probe. All spectra were measured at an ion source temperature of 200 °C or less and an ionization energy of 70 eV.

Preparation and Characterization of the Compounds. $\mathbf{Os_2N(S_2CNR_2)_5}$**, Where R =** $\mathbf{CH_3}$ **or** $\mathbf{C_2H_5}$**.** In an attempt to synthesize new osmium dithiocarbamato complexes, the reaction between $OsCl_3 \cdot xH_2O$ (ROC/RIC) and $Na(R_2dtc)$, where R = CH_3 or C_2H_5, was carried out in refluxing CH_3CN solution for 1 h under a N_2 atmosphere. Column chromatography of the residue using alumina for R = CH_3 and silica gel for R = C_2H_5 and CH_2Cl_2 as eluent gave a 70% yield of an orange-brown complex. Crystallization was achieved from CH_2Cl_2–heptane. The compounds are diamagnetic in solid and solution, nonconducting in nitromethane at 25 °C ($\Lambda = 0.35$ and 0.56 Ω^{-1} cm^2 mol^{-1} for R = CH_3 and C_2H_5, respectively), and benzene soluble and the R = CH_3 compound has five equally intense singlet ^1H NMR signals (τ (in CD_2Cl_2 solvent) 6.25, 6.68, 6.73, 6.74, 6.79).