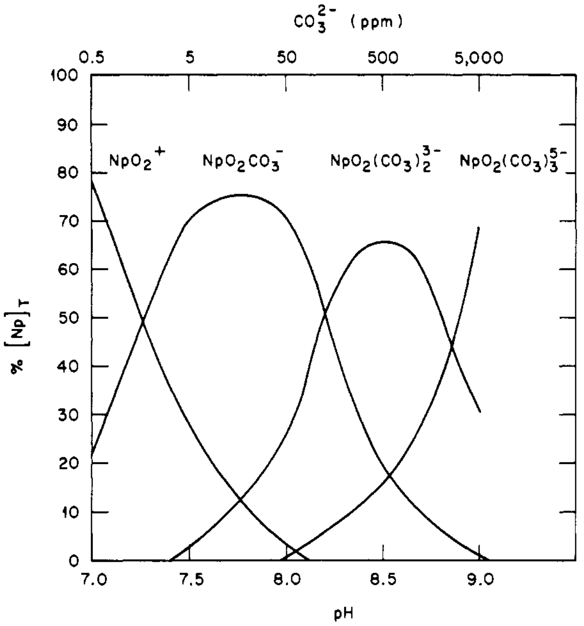

Figure 2. Neptunium(V) speciation scheme under a carbon dioxide partial pressure of $10^{-2.0}$ atm.

to the triply charged $NpO_2(CO_3)_2^{3-}$ ion. The reliability of the log β_{13} value found in this work can be further assessed from the following discussion. The $E_{1/2}$ value of the Np(VI/V) couple in carbonate media was found to be constant in the range 0.1–3.0 M Na_2CO_3.[9] This was also observed by Wester and Sullivan[10] in bicarbonate–carbonate solutions in the pH range 8.3–11.2. This behavior indicates an unchanging number of carbonate ligands for Np(V) and Np(VI), which is three according to observations made by Simakin[9] based on the solubility behavior of $Na_3NpO_2(CO_3)_2$ in carbonate media. The stability constant found in this work would also predict that $NpO_2(CO_3)_3^{5-}$ is the dominant species of Np(V) at $[CO_3^{2-}] \geq 0.1$ M. The $E_{1/2}$ value of the Np(VI/V) couple in carbonate media is 0.7 V more negative than that of this couple in a noncomplexing medium.[11] This indicates that the log β_{13} value of the VI species is larger by 11.84 than that of the V species. Using this value and that of log β_{13} for the Np(V) species found in this work gives an estimate of 20.37 for log β_{13} of Np(VI). This estimate is quite reasonable when it is considered that the corresponding log β_{13} value for U(VI) is 21.81.[12] Comparable differences are observed between U(VI) and Np(VI) hydrolytic constants; the value of $-\log \beta_{35}$ is 15.6 for U(VI) and 17.5 for Np(VI).[13] Finally, an additional measure of confidence is derived from the fact that Q_H, as found in this work, is very close to that estimated by Kraus and Nelson.[3]

Raman spectra of the solid used in this study were obtained to further characterize this material. The main features in the spectra of $NaNpO_2CO_3 \cdot 3.5H_2O$ are the bands due to ν_1 vibrations of the NpO_2 moiety at 775 cm^{-1} and those of CO_3, ν_1 at 1100 cm^{-1} and ν_3 at 1404 and 1569 cm^{-1}. The 775-cm^{-1} frequency of the neptunyl symmetric stretch in this compound is similar to that for $Na_3NpO_2(CO_3)_2$, which is 772 cm^{-1}.[14] That such a similarity can occur between these two compounds, in spite of the different stoichiometry, is apparently a consequence of the very similar environments of the NpO_2 moiety in the respective crystal structures as described by Volkov et al.[15] The CO_3 ν_1 band (1100 cm^{-1}) has a higher frequency than that commonly observed for complexed CO_3^{2-}, which is about 1070 cm^{-1}.[16] The $\nu_1(CO_3)$ band in $NaNpO_2CO_3 \cdot 3.5H_2O$ is closer to those of magnesite or dolomite, found respectively at 1096 and 1099 cm^{-1}.[16] This perhaps reflects the ionic character of the lattice, with independent NpO_2 and CO_3 units. On the other hand, the presence of a split ν_3 vibration for CO_3 indicates some degree of coordination between the neptunyl and carbonate moieties. The splitting is less pronounced than that observed in $Na_4UO_2(CO_3)_3$, 1358 and 1630 cm^{-1}.[17] This uranium salt contains distinct $UO_2(CO_3)_3$ moieties as shown by the crystal structure of the related ammonium salt.[18] It appears, then, that the bonding in the neptunium compound is intermediate between a completely ionic structure and one containing definite dioxoneptunium carbonato anions.

The carbonate complexation constants and the hydrolytic constants found in this work were used to calculate a species distribution scheme for Np(V) in the pH range 7.0–9.0 under a partial CO_2 pressure of $10^{-2.0}$ atm. The results are shown in Figure 2. It was found that under the most likely conditions to be found in nature the dominant species would be $NpO_2CO_3^-$ and/or $NpO_2(CO_3)_2^{3-}$. Formation of $NpO_2(CO_3)_3^{5-}$ would require relatively high CO_3^{2-} concentrations, which in turn would require an unusually high degree of oversaturation by the common carbonate minerals. Formation of $NpO_2OH(aq)$ is not favored unless the source of alkalinity in a groundwater is not associated with carbonate ions.

Conclusions

Neptunium(V), in spiite of its general tendency to form weak complexes, forms relatively stable carbonato complexes. This leads to the prediction that this element, under most conditions found in groundwaters, would be present in a complexed form. This finding is of importance in predicting the transport characteristics of this element.

Acknowledgment. I am very grateful to R. G. Haire and G. M. Begun for obtaining the X-ray and Raman spectroscopy data. I wish to thank J. Halperin for valuable discussions. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corp.

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New Five- and Six-Membered Saturated Heterocycles Containing Sulfur–Nitrogen Bonds

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and Herbert W. Roesky*[2]

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Following the pioneering work of Becke-Goehring et al.,[3] there has been a steadily growing interest in sulfur–nitrogen

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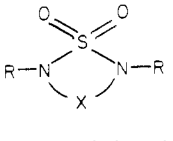
chemistry.[4] These efforts, spurred on more recently by interest in the solid-state properties of $(SN)_x$,[5] have culminated in the synthesis and structural assay of a wide variety of mono- and bicyclic ring systems incorporating sulfur–nitrogen bonds. The focus of the present work is the synthesis of ring systems featuring the $RNSO_2NR$ moiety, viz.



Four-, six-, and eight-membered rings have been reported with X = B,[6] C_2N,[7] Si,[8] P,[9] As,[10] S_2N,[11] S,[11] and S_3N_2.[11] Here we report the synthesis of new ring systems with X = C_2, CS, and Si_2O. The significance of the C_2 and CS rings is that they represent the first examples of saturated five-membered rings.

Experimental Section

Materials, General Procedures, and Spectroscopic Measurements. The sulfamides[12] $O_2S(MeNH)_2$ and $O_2S(EtNH)_2$ and the sulfenyl chloride[13] ClC(O)SCl were prepared according to literature methods. Other compounds were procured commercially. All solvents were carefully dried prior to use, and all operations were performed under an atmosphere of dry nitrogen.

The ^1H NMR spectra were recorded on a Varian XL-100 spectrometer (100 MHz), IR spectra were recorded on a Perkin-Elmer 157 spectrophotometer, and mass spectral data were acquired on a Varian CH 7 instrument at an ionizing voltage of 70 eV. Elemental analyses were performed by Mikroanalytischen Labor Beller, Göttingen, West Germany.

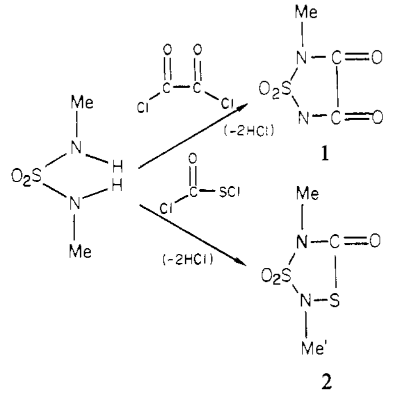
Preparation of $O_2S(MeN)_2(CO)_2$ (1). An excess of Et_3N (5.0 g) was added to a solution of 2.5 g (20.1 mmol) of $O_2S(MeNH)_2$ in 40 mL of C_6H_6 in a 100-mL two-necked flask equipped with a dropping funnel and reflux condenser. To this magnetically stirred solution was added dropwise a solution of 2.6 g (20.5 mmol) of $C_2O_2Cl_2$ in 30 mL of C_6H_6. An exothermic reaction took place. After the addition was complete, the reaction mixture was refluxed for 4 h. Filtration of the white solid $[Et_3NH]^+Cl^-$, followed by removal of the volatiles, left yellow, solid **1**. Recrystallization of the crude material from CH_2Cl_2/n-hexane at low temperature afforded 2.9 g (80.5% yield) of pure **1**, an air-stable white crystalline solid, mp 118–119 °C. Anal. Calcd for $C_4H_6N_2SO_4$: C, 27.0; H, 3.4; S, 18.0. Found: C, 27.2; H, 3.5; S, 17.9. The mass spectrum contains a parent peak at m/e = 178. The base peak appears at m/e = 57 and is attributable to $[MeNCO]^+$. IR: ν_{CO} = 1800, 1760 cm^{-1}; ν_{SO_2} = 1180, 1285 cm^{-1}; ν_{NSN} = 935 cm^{-1}. ^1H NMR (CH_2Cl_2): (s, δ 3.67).

Preparation of $O_2S(MeN)_2SC(O)$ (2). With use of a procedure similar to that described for the synthesis of **1**, a solution of 4.0 g of Et_3N and 2.11 g (16.9 mmol) of $O_2S(MeNH)_2$ in 40 mL of C_6H_6 was treated with 2.3 g (17.6 mmol) of ClC(O)SCl in 30 mL of C_6H_6. An exothermic reaction took place. Filtration, followed by removal of the volatiles, left a yellow oil. Distillation of the yellow oil (bp 69–73 °C at 10^{-2} torr) afforded 1.22 g (40.0% yield) of **2**. Anal. Calcd for $C_3H_6N_2O_3S_2$: C, 19.8; H, 3.3. Found: C, 21.7, H, 3.8. Compound **2**, a yellow liquid, undergoes decomposition upon standing at room temperature for 1–2 days, thus explaining the poor analytical data. However, the spectroscopic data leave no doubt regarding the identitiy of the compound. Thus, the mass spectrum features a parent peak at m/e = 182. Fragmentation peaks of significant intensity appear at m/e = 93 and 61 and are assignable to $[MeNSO_2]^+$ and $[MeNS]^+$, respectively. Moreover, the presence of CO and NSN moieties is indicated by the presence of ν_{CO} and ν_{NSN} at 1720 and 885 cm^{-1}, respectively, in the IR spectrum. The SO_2 stretching vibrations occur at 1195 and 1270 cm^{-1}. As expected, the Me groups are nonequivalent in the ^1H NMR spectrum. ^1H NMR (neat): NMe (s, δ 3.41), NMe′ (s, δ 3.38).

Preparation of $O_2S(EtN)_2(SiMe_2)_2O$ (3). With use of a procedure similar to that described for the synthesis of **1**, a solution of 4.0 g of Et_3N and 2.4 g (15.8 mmol) of $O_2S(EtNH)_2$ in 40 mL of Et_2O was treated with 3.2 g (15.2 mmol) of $(ClSiMe_2)_2O$ in 30 mL of Et_2O. Following the exothermic reaction, the mixture was refluxed for 4 h. After the volatiles were stripped, the resulting distillation gave **3** (bp 71 °C at 10^{-2} torr). The yield of pure **3**, a moisture-sensitive yellow liquid, was 78.6% (3.5 g). Anal. Calcd for $C_8H_{22}N_2O_3SSi_2$: C, 34.0; H, 7.8; N, 9.9; S, 11.4. Found: C, 33.3; H, 7.5; N, 9.7; S, 11.1. The mass spectrum exhibits a parent peak at m/e = 282. The base peak appears at m/e = 267 and is attributable to $(M - Me)^+$. IR: ν_{SO_2} = 1175, 1265 cm^{-1}; ν_{NSN} = 920 cm^{-1}; ν_{SiOSi} = 1340 cm^{-1}. ^1H NMR (CH_2Cl_2): Me_2Si (s, δ 0.34), $NCH_2C\mathit{H}_3$ (t, δ 1.18, J_{HCCH} = 7.0 Hz), $NC\mathit{H}_2CH_3$ (q, δ 3.22, J_{HCCH} = 7.0 Hz).

Results and Discussion

2,5-Dimethyl-1-thia-2,5-diazolidine-3,4-dione 1,1-dioxide (**1**) and 2,5-dimethyl-1,4-dithia-2,5-diazolidin-3-one 1,1-dioxide (**2**) have been prepared by the reaction of the sulfamide $(MeNH)_2SO_2$ with oxalyl chloride and (chlorocarbonyl)sulfenyl chloride, respectively, in the presence of Et_3N (eq 1).



(1)

Compound **1** is an air-stable white solid and **2** is a yellow liquid that decomposes on standing at room temperature. Both compounds were characterized by elemental analysis and IR, ^1H NMR, and mass spectroscopy (Experimental Section). To the best of our knowledge, these compounds represent the first examples of saturated SN_2C_2 and S_2N_2C ring systems. Previous examples of these ring systems (**4**–**6**) involved unsaturation.

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(2) Universität Göttingen.

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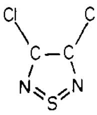

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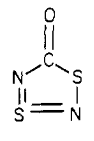

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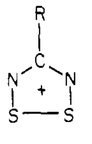

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Registry No. **1**, 55904-82-0; **2**, 85662-25-5; **3**, 85662-26-6; $(MeNH)_2SO_2$, 22504-72-9; $O_2S(EtNH)_2$, 6104-21-8; $(ClSiMe_2)_2O$, 2401-73-2; oxalyl chloride, 79-37-8; (chlorocarbonyl)sulfenyl chloride, 2757-23-5.

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ESR Investigation of the Rearrangement of a Heterobimetallic (Co/Mo) Dioxygen Complex. Characterization of a ·CN Free Radical

Henri Arzoumanian,* Richard Laï, Jacques Metzger, Jean-François Pêtrignani, and Paul Tordo

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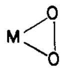
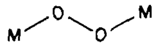
A great number of dioxygen complexes of transition metals have been synthesized as either peroxo

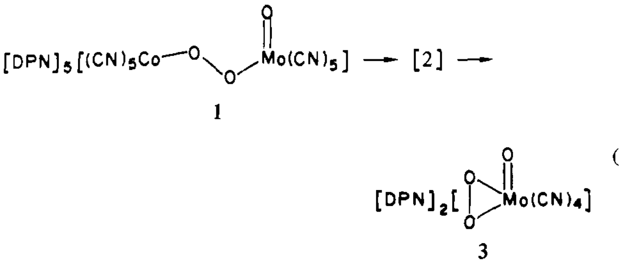


or μ-peroxo



compounds.[1] The study of their reactivity has furthermore suggested that they are key intermediates in selective catalytic oxidations, when dioxygen is the oxidizing agent.[2] Many homogeneous[3] or heterogeneous[4] catalytic autoxidation processes, however, involve more than one type of metal. This led us to synthesize a heterobimetallic dioxygen complex in order to study the transfer of the dioxygen moiety from one metal center to the other in a multistep activation[5] of O_2.

In the course of a study[6] of the rearrangement of such a complex (Co/Mo), an oxygen-18 labeling experiment suggested strongly the intermediacy of a molybdenum(V) compound[7] (**2**) able to react directly with dioxygen (eq 1).



$$[\mathrm{DPN}]_5[(\mathrm{CN})_5\mathrm{Co{-}O{-}O{-}Mo(O)(CN)_5}] \rightarrow [2] \rightarrow [\mathrm{DPN}]_2[\mathrm{(O_2)Mo(O)(CN)_4}] \qquad (1)$$

$$\mathrm{DPN} = [(\mathrm{PPh_3})_2\mathrm{N}]^+$$

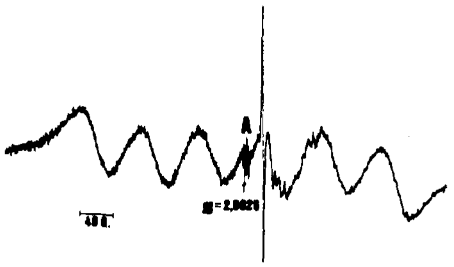


Figure 1. ESR signal obtained by reacting compound **1** with dioxygen in CH_2Cl_2.

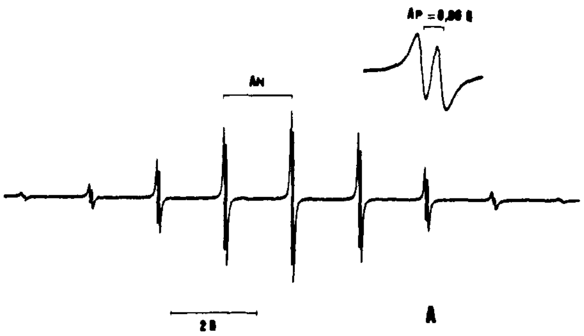


Figure 2. ESR signal of $TCNE^-$ (A in Figure 1) showing a small phosphorus splitting from the bis(triphenylphosphine)nitrogen(1+) cation.

The importance of this unprecedented observation brought us to investigate its mechanism by carrying out an ESR investigation.

Experimental Section

Bis(triphenylphosphine)nitrogen(1+) (μ-peroxo)pentacyanocobaltate(III) oxoaquopentacyanomolybdate(VI) (**1**) and bis(triphenylphosphine)nitrogen(1+) oxoperoxotetracyanomolybdate(VI) (**3**) were prepared as reported.[6,7] All solvents were reagent grade and thoroughly dried and degassed prior to use.

The ESR spectra were obtained on an X-band Varian Model E 109 spectrometer, at 25 °C with a cavity frequency of 8.9 GHz. The field was 3200 G, and the cavity of the spectrometer is a E.238 T M_{110}.

The sample solutions were prepared with solvents thoroughly degassed on a vacuum line. Oxygen was introduced when it was desired by opening the system to air or pure oxygen atmosphere.

Thermolysis of *tert*-butyl peroxalate $(t\text{-BuOOCO})_2$ was used to produce *tert*-butoxyl radicals during the generation of the "authentic" nitroxide 7.

Results and Discussion

A methylene chloride solution of complex **1** in a strictly oxygen-free atmosphere shows no significant ESR signals even for long periods of time.

When the green solution is allowed to get in contact with air or oxygen, it becomes yellow and exhibits the ESR signals presented in Figure 1. The six broad bands (A_X = 70 G, $g \simeq 2.0026$) characteristics of the coupling of the unpaired electron with a spin $^5/_2$ nucleus cannot be unambiguously assigned.[8]

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