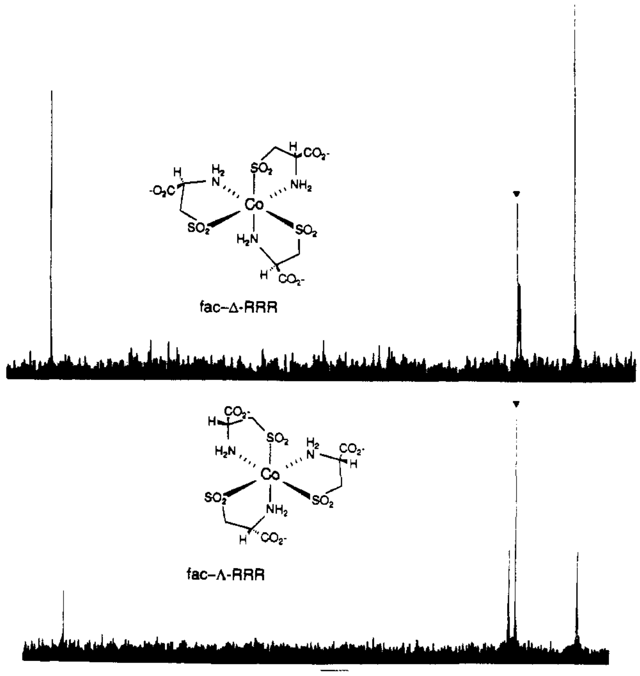

Figure 2. ^{13}C NMR spectra for Δ-$[Co((R)\text{-cysSO}_2\text{-}N,S)_3]^{3-}$ (upper spectrum) and Λ-$[Co((R)\text{-cysSO}_2\text{-}N,S)_3]^{3-}$ (lower spectrum) in D_2O (25 °C). Shifts are given in ref 16; ▼ denotes the reference signal.

was indeed pure, and not a Δ-*RRR*/Λ-*RRR* mixture that on dissolution had all isomerized to Δ-*RRR*.

It is now clear that, irrespective of which isomer or stoichiometric isomer mixture crystallizes preferentially, the Δ-*RRR* isomer is the much more abundant under equilibrium conditions—we could detect no Λ-*RRR* isomer by ^{13}C NMR spectroscopy. The Δ assignment is based on that predicted to be the more stable (the $(lel)_3$ form)[10,11] by methods shown experimentally to be reliable with, for example, the well-studied $[Co((R)\text{-pn})_3]^{3+}$ system. Perhaps ironically, it is the same isomer that Gillard and Maskill[12] isolated as the potassium salt and claimed to be that formed stereospecifically, although their conclusions were erroneously based on observations on the isomeric composition of isolated material. This does not necessarily relate to the equilibrium solution composition, as demonstrated in this work.

The related methyl ester cysteine complex $K_3[Co((R)\text{-MecysS})_3]\cdot H_2O$ has been synthesized, and it has been assumed that it resembles the cysteine analogue and is formed stereospecifically.[6] Athough its peroxide oxidation products were separated chromatographically and characterized by ^{13}C NMR and CD spectroscopic measurements, the starting material was not, and therefore there is no clear way of knowing if the various sulfenato products differ in the absolute configuration at sulfur or cobalt or both. The peroxidized tris(cysteinesulfinate) species, after hydrolysis of the ester groups, was similar in optical properties to the authentic Δ-*fac-RRR* isomer, suggesting that the starting material may have been a single isomer, but with no yield reported for the synthesis the claim to a stereospecific synthesis[6] cannot be upheld.

Finally, Dollimore and Gillard[14] have used the yellow $[Co((R)\text{-cysSO}_2\text{-}N,S)_3]^{3-}$ anion, first obtained by Schubert,[2] to optically resolve a number of cationic coordination complexes. Since this complex is made directly from the tris(cysteinate) by peroxidation, a reaction that does not affect the chirality at cobalt, one would reasonably suspect that the geometry of this complex would reflect that of its precursor. In view of our findings for the tris(cysteine) species, the Δ isomer, the Λ isomer, or a mixture might be obtained depending upon the configuration of the starting material and the conditions of crystallization. Accordingly, we have repeated Dollimore and Gillard's experiments[14] using not only the Δ form but also the Λ isomer and the stoichiometric 1:1 mixture as the substrates. We obtain the same less soluble material (Figure 2, upper spectrum) from the syntheses using Δ or the Δ/Λ mixture; it crystallizes as fibrous needles from H_2O/ethanol, and the ORD and CD spectra establish that it is the same isomer which was described by Dollimore and Gillard and which they (correctly) assigned as Δ.[12,14] (The ^{13}C NMR spectrum[16] has not been published previously, but Gillard[21] has described it as "remarkably simple".) The material obtained from the Λ starting material is quite different, and must be the corresponding Λ isomer (Figure 2, lower spectrum), a new substance. As the Ba^{2+} salts, the Δ isomer was much less soluble than the Λ isomer, accounting for their ready separation above, and there no longer seems to be a facile thermal or catalytic path to equilibrate the isomers.

The inference is that if one intends to use the Δ tris(cysteinate) trianion as a resolving agent, the material should be carefully recrystallized to remove the more soluble Λ form (as K^+ or Ba^{2+} salts), which may well have been present. Also the material should be routinely checked for the presence of the other diastereomer by a technique such as ^{13}C NMR spectroscopy.

Experimental Section

The basic starting complexes, which include $K_3[Co((R)\text{-cysS-}N,S)_3]\cdot 3H_2O$, $Na[Co(OCO)_2)_3]\cdot 3H_2O$, *trans*-$[Co(py)_4Cl_2]Cl\cdot 6H_2O$, and $K[Co(edta)]\cdot 2H_2O$, were prepared as described in the literature.[2,22-24] The several barium salts of $[Co((R)\text{-cysS-}N,S)_3]^{3-}$ were obtained as follows. By the slow addition of a strong aqueous $BaCl_2$ solution to one of the potassium salt containing a little KOH, at ambient temperature, gray fibrous needles were readily deposited (Δ isomer, $Ba_3[Co(R)\text{-cysS-}N,S)_3]_2\cdot 7H_2O$). These were collected immediately, washed with ice water, ethanol, and ether, and air-dried. In a separate preparation, these crystals transformed to darker granular crystals on prolonged gentle warming (ca. 60 °C); shortly after this phase change, the crystals were collected and washed and dried as above (1:1 Δ:Λ phase, $Ba_3[Co((R)\text{-cysS-}N,S)_3]_2\cdot 7H_2O$). In yet another separate synthesis, these crystals were allowed to stir at ambient temperature for several hours; fine dull green crystals resulted (Λ isomer, $Ba_3[Co((R)\text{-cysS-}N,S)_3]_2\cdot 7H_2O$). The H_2O_2 oxidations of the K^+ and Ba^{2+} salts were carried out as described[14] at ca. 5 °C with 30% H_2O_2. The products have the stoichiometry $K_3[Co((R)\text{-cysSO}_2\text{-}N,S)_3]\cdot 3H_2O$ and $Ba_3[Co((R)\text{-cysSO}_2\text{-}N,S)_3]_2\cdot 6H_2O$. The insoluble Ba^{2+} salts of the reactants dissolved readily as the sulfenate complexes formed but crystallized essentially quantitatively when the insoluble tris(sulfinate) species finally resulted. The recrystallization included a fine-porosity filtration step to remove a decomposition product resulting from the H_2O_2 oxidation procedure. The K^+ and Ba^{2+} salts of $[Co((R)\text{-cysS-}N,S)_3]^{3-}$ and $[Co((R)\text{-cysSO}_2\text{-}N,S)_3]^{3-}$ were fractionally crystallized from water/ethanol. Carbon-13 NMR spectra (18 °C) were obtained on a Varian XL 300 instrument using dioxane as the internal reference. Slurries of the insoluble Ba^{2+} salts in D_2O were treated with 1.5 equiv of K_2SO_4 to effect dissolution and then centrifuged or filtered prior to the NMR experiments.

Acknowledgment. This work was supported by grants to A.P.A. and W.G.J. from the Australian Research Council.

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A Note on Symmetry and the Single-Crystal NMR Shift Tensor of the $CdCl_2\cdot$18-Crown-6 Complex

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Received March 20, 1990

Kennedy, Ellis, and Jakobsen recently determined the single-crystal NMR shift tensor for cadmium in $CdCl_2\cdot$18-crown-6,[1] whose crystal structure was determined by Paige and Richardson.[2]

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0020-1669/90/1329-3620$02.50/0

There are errors in the NMR parameters reported[1] since the authors did not take into account the high symmetry of the cadmium.

The cadmium occupies one of the $\bar{3}$ (C_{3i}) special positions in the rhombohedral space group $R\bar{3}$, on the 3-fold xis of the unit cell.[2] This *requires* that the NMR shift tensor be axially symmetric ($\sigma_{11} = \sigma_{22}$) with one axis of the tensor (σ_{33}) aligned along the 3-fold axis.[3] The directions of the x and y axes are not uniquely defined when axial symmetry is present; any pair of orthogonal axes that are also orthogonal to the z axis will serve.[4] The symmetry also requires that the NMR chemical shifts determined by rotations about the rhombohedral a, b, and c axes be identical. The fact that Kennedy, Ellis, and Jakobsen found that σ_{33} was 2.4° away from the 3-fold axis and that $\sigma_{11} = 414$ ppm while $\sigma_{22} = 385$ ppm actually represents a measure of the various errors associated with the experiment rather than any real differences in the σ_{11} and σ_{22} parameters.

The NMR measurements in this particular case can be greatly simplified by choosing an alignment based on hexagonal rather than rhombohedral axes.[5] In the hexagonal setting, the z axis of the tensor is coincident with the c axis of the hexagonal unit cell, and the x and y components of the tensor are perpendicular to it. Thus only two measurements are necessary to obtain the tensor components, the chemical shifts when the c axis is parallel to the applied field and when it is perpendicular to it.

Acknowledgment. I thank Prof. J. S. Hartman for helpful discussions.

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A New Synthesis of Xenon Oxytetrafluoride, $XeOF_4$

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Received June 23, 1989

There has been continued interest in xenon fluorides to increase the knowledge of the bonding and reactivity of noble gas compounds. Reported syntheses of xenon fluorides and oxyfluorides can be less than safe and in some instances very hazardous. For example, one common preparation of $XeOF_4$ involves partial hydrolysis of XeF_6 in either a static or dynamic system. The dynamic method, a controlled hydrolysis, involves a complex setup to monitor the decrease in the XeF_6 concentration in a flow loop while air is bled into the system.[1] The static method, accomplished by reacting XeF_6 with either SiO_2 or H_2O, can be quite dangerous due to inadvertent formation of highly explosive XeO_3.[2] Another method uses SeO_2F_2 as an oxygen source but suffers from the high toxicity and difficult preparation of SeO_2F_2.[3] Recently, Christe and Wilson reported that $XeOF_4$ can be prepared in high yields from readily available reagents through the reaction of XeF_6 with $NaNO_3$.[4] However, if an excess of $NaNO_3$ is used, $XeOF_4$ further reacts with $NaNO_3$ to give XeO_2F_2.[5] We report a new synthetic method for preparing $XeOF_4$ in nearly quantitative yield that reduces the problem of XeO_3 formation.

Experimental Section

Caution! The reaction of XeF_6 or $XeOF_4$ with an excess of $P(O)F_3$ can lead to the formation of explosive XeO_3. Care must be used when performing this procedure to ensure that an excess of $P(O)F_3$ is not used. Small amounts of all reagents should be used in order to minimize risk of explosions and damage, and appropriate safety precautions should be taken. Xenon hexafluoride is a potent oxidizer that readily hydrolyzes to explosive XeO_3.

Materials and Apparatus. Xenon (Matheson Corp.) was used as received. Xenon hexafluoride, XeF_6, was prepared by the method of Chernick and Malm from Xe and excess F_2 in the presence of NaF followed by vacuum pyrolysis of the adduct $NaXeF_7$.[6] Phosphoryl fluoride, $P(O)F_3$, was prepared by the reaction of SbF_3 and $P(O)Cl_3$ and purified by vacuum distillation.[7] Volatile materials were manipulated in a stainless steel vacuum line equipped with Kel-F and stainless steel traps, Autoclave Engineers valves, and MKS and Helicoid pressure gauges. Prior to use, the vacuum line was thoroughly passivated with ClF_3 and XeF_6 followed by overnight evacuation. Nonvolatile materials were handled in a dry He atmosphere glovebox. Infrared spectra of volatile materials were recorded on a Perkin-Elmer 1500 FTIR spectrometer using a 10-cm stainless steel cell fitted with AgCl windows.

Preparation of $XeOF_4$. Xenon hexafluoride (1.2 g, 4.9 mmol) followed by 0.52 g (4.9 mmol) of $P(O)F_3$ at −196 °C was condensed into a Kel-F reaction tube. The reaction vessel was allowed to warm slowly to room temperature, and within 5 min the solid XeF_6 began to evolve gas and liquefy. After 2 h at room temperature, the contents of the reactor were vacuum-transferred to a 30-mL stainless steel cylinder containing dried NaF to remove PF_5. After several hours at room temperature in contact with NaF, the volatile material was removed from the cylinder and identified as pure $XeOF_4$ (1.1 g, 4.9 mmol) by its infrared spectrum[8] and room-temperature vapor pressure.[1] The NaF scrubber retained 0.59 g (4.7 mmol) of complexed PF_5. Alternately, the PF_5 may be more rapidly removed by vacuum distillation from the mixture using a trap held at −55 °C.

Results and Discussion

The reaction of $P(O)F_3$ and XeF_6 provides a very convenient, high-yield, fast synthesis of $XeOF_4$. The oxygenating agent ($P(O)F_3$) is easily prepared in quantity from readily available materials, is anhydrous as prepared, and is easily handled in vacuum systems, allowing for precise and accurate measurement of small quantities. The only byproduct of the reaction (PF_5) is easily separated from $XeOF_4$ on the basis of either its greater volatility or its stronger Lewis acidity (toward NaF). It is not necessary to use a large excess of XeF_6 to avoid formation of significant amounts of treacherous XeO_3, since $XeOF_4$ reacts much more slowly with $P(O)F_3$ than does XeF_6. This was demonstrated by the reaction of $P(O)F_3$ with $XeOF_4$ in a 1:1 ratio. After this reaction was allowed to proceed for 4 days followed by removal of volatiles (unreacted $XeOF_4$, $P(O)F_3$, and PF_5), only a small amount of white solid (less than 0.05 g) was recovered. During an attempt to identify this material, an explosion occurred and the material, on the basis of its detonability and lack of volatility, was presumed to be either XeO_2F_2 or XeO_3. Explosions can be avoided if $P(O)F_3$ and XeF_6 are reacted in a ratio close to 1:1 and a short reaction time is used. Separation of the resulting products is simple. When the reaction is performed in the prescribed manner, the products are all gases or volatile liquids and fractional condensation through two traps kept at −55 and −196 °C cleanly separates $XeOF_4$ from PF_5 and $P(O)F_3$ and gives spectroscopically pure $XeOF_4$ in quantitative yield. If a slight excess of XeF_6 is used, purification may be accomplished by placing the contents of the reaction over NaF to complex PF_5 and XeF_6.

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