easy synthetic routes to a few species otherwise difficult to obtain.

Experimental Section

Standard high-vacuum line techniques were employed to handle all volatile compounds. Moisture-sensitive solids were manipulated under nitrogen in a drybox. Infrared spectra of the solid samples as KBr pellets were recorded on Beckman Acculab 4 and Perkin-Elmer 621 spectrometers. Raman spectra of the solid products and liquid SO_2 or CH_3CN solutions were observed with a Jarrell-Ash 25-300 Raman spectrometer with excitation by the 514.5-nm line of an argon ion-laser. Fluorine resonance spectra of the SO_2 and CH_3CN solutions were obtained with a Varian Associates XL-100 spectrometer with a Nicolet Fourier transform attachment at 94.1 MHz. Chemical shifts, positive to low field, are referenced to $CFCl_3$ as internal standard. X-ray powder diffraction patterns were taken with Cu radiation in 114-mm diameter Debye–Scherrer cameras. Tungsten hexafluoride (Ozark-Mahoning), uranium hexafluoride (Varlacoid), molybdenum hexafluoride (Cerac), and tellurium and selenium hexafluorides (Ozark-Mahoning) were used as received. Lithium, cesium, and tetramethylammonium (TMA) azides were prepared from the corresponding hydroxide and hydrazoic acid, while sodium azide was a commercial product. Sulfur dioxide and acetonitrile were dried by repeated distillation over P_2O_5.

Synthesis of WF_5N_3 and $CsWF_7$. A total of 0.0265 g of vacuum-dried cesium azide was dissolved in 0.67 g of anhydrous sulfur dioxide, and a threefold excess of tungsten hexafluoride (0.157 g) was added. The reagents reacted together to give a yellow solution and a white precipitate. The solution was decanted to a side arm and the precipitate washed by distillation of SO_2 from the solution onto it followed by decantation. All readily volatile materials were removed by pumping under vacuum to yield 0.0655 g (96%) of $CsWF_7$ and 0.0488 g (100%) of WF_5N_3. The identity of the $CsWF_7$ was confirmed by the identity of its Raman spectrum and its X-ray powder pattern with those already reported.[4,5] WF_5N_3 was identified by its fluorine resonance spectrum ($\delta(F_{eq}) = 137.4$, $\delta(F_{ax}) = 100.1$, $J_{F-F} = 73.0$ Hz, $J_{W-F_{eq}} = 36.9$ Hz) and Raman spectrum. It is shock and moisture sensitive and must be handled with care.

Synthesis of $CsUF_6$. A total of 0.0309 g of vacuum-dried CsN_3 dissolved in 0.64 g of anhydrous sulfur dioxide was mixed with 0.0736 g of UF_6. Vigorous evolution of nitrogen commenced immediately. All volatile materials were removed under vacuum to give 0.0875 g of $CsUF_6$. Its identity was confirmed by X-ray powder diffraction[6] and elemental analysis. Anal. Calcd: Cs, 27.4; U, 49.1; F, 23.5. Found: Cs, 27.5; U, 46.6; F, 22.3.

Synthesis of $TMAMoF_6$. A total of 0.1069 g of vacuum-dried $TMAN_3$ dissolved in 1.048 g of anhydrous sulfur dioxide was mixed with 0.195 g of MoF_6 and the solution, initially blood red, allowed to warm to room temperature. The solution turned pale orange and evolved 1.32 mmol of nitrogen gas (theoretical 1.38 mmol). All volatile materials were removed under vacuum to give 0.2626 g of $TMAMoF_6$ (theoretical 0.2616 g). Anal. Calcd: Mo, 33.8; F, 40.1. Found: Mo, 33.2; F, 39.4.

Results and Discussion

The reactions of tungsten, molybdenum, and uranium hexafluorides with azide ion may be described by eq 1–3.

$$MF_6 + N_3^- \rightarrow MF_6N_3^- \qquad (1)$$

$$2MF_6 + N_3^- \rightarrow MF_7^- + MF_5N_3 \qquad (2)$$

$$MF_6 + N_3^- \rightarrow MF_6^- + {}^3/{}_2N_2 \qquad (3)$$

Reaction 1 is the predominant reaction with WF_6 and tetramethyl- or tetrabutylammonium azide in SO_2 or CH_2Cl_2 as solvent although the products of reaction 2 are produced slowly and to a slight extent when more than 1 equiv of WF_6 is initially present in the reaction mixture.[7] It has also been shown that there is rapid exchange via a displacement mechanism between free and complexed WF_6.[7] With lithium, sodium, and cesium azides and WF_6 only products specified by reaction 2 are observed with sulfur dioxide as solvent. In the cases of Li and Na pure MWF_7 cannot be isolated since it gradually decomposes to MF and WF_6. In acetonitrile as solvent reaction 1 occurs rapidly with Li, Na, Cs, and TMA azide followed by a slow reaction (eq 3) causing evolution of nitrogen. It is therefore possible to synthesize pure $CsWF_7$ and WF_5N_3 but not MWF_6 since reaction 3 is slow.

The reaction of UF_6 with azide ion may be described by eq 3 in every case. In SO_2 as solvent complete reaction occurs with cesium and tetramethylammonium as cations. With lithium and sodium as cations and 1 equiv of UF_6 reaction is slow, is incomplete, and depends upon the state of aggregation of the azide. In the presence of an excess of UF_6 the reaction is more vigorous. However it is possible to have complete reaction of Li and NaN_3 by conducting the reaction in acetonitrile as solvent, where reaction 3 proceeds smoothly with an excess of UF_6. The reaction of MoF_6 with azide ion is described by eq 3. TeF_6 reacts with $TMAN_3$ slowly and incompletely in SO_2 solution to give many fluorine containing species. SeF_6 does not react with $TMAN_3$ under similar conditions.

A somewhat analogous situation is the reaction of trimethylsilyl azide with hexafluorides. The reaction of WF_6 to yield WF_5N_3 has already been described.[3] With UF_6 there is evolution of nitrogen, and the only fluorinated species observed by fluorine resonance spectroscopy is trimethylsilyl fluoride. Similar results are observed in the room-temperature reaction with MoF_6, however at −70 °C a doublet and quintuplet are found in the fluorine resonance from MoF_5N_3 (δ 182.4 and 237.6, $J = 94.4$ Hz) and a pair of triplets from *cis*-$MoF_4(N_3)_2$ (δ 147.1 and 179.0, $J = 91.1$ Hz). These chemical shifts are consistent with those predicted by the equation $\delta(F) = pC + qT$ for substituted octahedral fluorinated species[8] and the magnitudes of C and T are appropriate.[1]

Registry No. WF_5N_3, 75900-58-2; $CsWF_7$, 57373-25-8; CSUF$_6$, 17374-59-3; $TMAMoF_6$, 78199-46-9; WF_6, 7783-82-6; UF_6, 7783-81-5; MoF_6, 7783-77-9; MoF_5N_3, 75900-59-3; *cis*-$MoF_4(N_3)_2$, 78198-91-1; N_3^-, 14343-69-2.

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Thermal Decomposition of $[Rh(NH_3)_5Cl]Cl_2$

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Recently Kohata and co-workers reported the preparation of $[Rh(NH_3)_4Cl_2]Cl$ by heating $[Rh(NH_3)_5Cl]Cl_2$ at 296 °C for 130 min to simply expel one molecule of ammonia from the latter complex.[1] We have studied the thermal decomposition of this compound under the same conditions as described by Kohata et al., with a substantially different outcome. We found that the thermal decomposition of this complex results in the formation of rhodium metal as well as $[Rh(NH_3)_4Cl_2]Cl$.

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Experimental Section

The experimental apparatus consists of a Du Pont 990 thermogravimetric analyzer coupled to a Metrohm automatic titrator for the quantitative analysis of evolved ammonia; previous uses of this instrument include the thermal decomposition of transition-metal ammines[2,3] and hexachloroplatinic acid.[4,5] Hydrogen and helium purge gases (99.99% min) were dried (5A molecular sieves) before use; purge-gas flow rates through the instrument were 120 mL/min. Pyrolysis runs were performed with a heating rate of 20 °C/min over the range 25–600 °C; for the isothermal runs, the sample was heated at 20 °C/min to the desired temperature. $[Rh(NH_3)_5Cl]Cl_2$ was synthesized by the procedure of Osborn et al.;[6] unless stated otherwise, 10–15-mg samples (previously ground to a fine powder) were used.

Results

The purity of the $[Rh(NH_3)_5Cl]Cl_2$ was determined by pyrolysis in hydrogen; this effected the reaction

$$2[Rh(NH_3)_5Cl]Cl_2 + 3H_2 \rightarrow 2Rh + 4NH_3 + 6NH_4Cl \qquad (1)$$

which occurred between 200 and 340 °C. The analysis was as follows: ash (assumed to be rhodium metal) found 33.99%, calcd 34.95%; mol of ammonia/mol of rhodium metal found 2.03, calcd 2.00; mol of ammonia chloride/mol of rhodium metal found 3.08, calcd 3.00.

Pyrolysis in helium over the temperature range of 280–390 °C occurred with reduction of rhodium(III) to the metal and concurrent oxidation of ammonia via the reaction

$$2[Rh(NH_3)_5Cl]Cl_2 \rightarrow 2Rh + 2NH_3 + 6NH_4Cl + N_2 \qquad (2)$$

We found the following results: ash (assumed to be rhodium metal) found 35.43%, calcd 34.95%; mol of ammonia/mol of rhodium metal found 1.07, calcd 1.00; mol of ammonium chloride/mol of rhodium metal found 2.98, calcd 3.00.

Under the conditions described by Kohata and co-workers we obtained only 0.68 mol of ammonia/mol of $[Rh(NH_3)_5Cl]Cl_2$, equivalent to 3.9% of the initial sample weight (12.70 mg), while the total weight loss of the sample was 22.9%. A significant quantity of ammonium chloride was observed on the wall of the cool exit end of the TGA reactor tube. These results clearly indicate that reaction 2 is occurring to a significant extent. However, if reaction 2 were the only reaction proceeding under our conditions, the weight loss due to ammonia should have been 1.9%. Thus, we conclude that reaction 2 and the decomposition of the pentaammine complex to produce $[Rh(NH_3)_4Cl_2]Cl$ are occurring simultaneously. We have observed that sample size does have an effect on the decomposition; for larger sample sizes (up to 61 mg), a smaller fraction of the weight loss is attributable to ammonia. A similar effect of sample size on the thermal decomposition of *trans*-$[Pd(NH_3)_2Cl_2]$ has been discussed.[3] Over the range of sample sizes (9–61 mg) and temperatures (280–296 °C) investigated, the total weight loss is always much greater than the weight of evolved ammonia. Our observations lead us to question the results of Kohata and co-workers, who had not thoroughly characterized their presumed $[Rh(NH_3)_4Cl_2]Cl$ product.

Registry No. $[Rh(NH_3)_5Cl]Cl_2$, 13820-95-6.

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Additions and Corrections

1981, Volume 20

Yu-Ying Chen, Doris E. Chu, Billy D. McKinney, Lawrence J. Willis, and Sue C. Cummings*: High-Spin, Five-Coordinate Complexes of Cobalt(II), Nickel(II), and Copper(II) with Linear, Pentadentate Keto Iminato Ligands.

Page 1891. Reference 32 is incorrect. It should read: Niswander, R. H.; Taylor, L. T. *Inorg. Chem.* **1976**, *15*, 2360–2364.

Pages 1885–1892. Variations in both a_{iso} and $a_\parallel$ correlate with differences in the strength of the axial interaction; however, the numerical values of the hyperfine splitting constants cited in the text are for a_{iso} (not $A_\parallel$).

Values of $g_\perp$ and $a_\perp$ for the (keto iminato)copper(II) complexes, as reported in Table VI, were calculated by using the equations $g_\perp = {}^1/_2(3g_{iso} - g_\parallel)$ and $a_\perp = {}^1/_2(3a_{iso} - a_\parallel)$. These values are clearly inconsistent with measured parameters, and they should be disregarded.

Alternative values of $g_\perp$ can be obtained in a few cases by approximating the midpoint between the maximum and minimum derivative signal, and values of $a_\perp$ can be obtained by dividing the difference between the maximum and minimum points by 3. Such an approach gives the following results: Cu(benacPhDPT), $g_\perp = 2.068$, $a_\perp = 37$; Cu(acacPhDPT), $g_\perp = 2.074$, $a_\perp = 41$; Cu(tfacPhDPT), $g_\perp = 2.092$, $a_\perp = 39$. Values for the MeDPT and DPT series of complexes could not be determined due to overlapping spectral patterns; however, in all cases $g_\parallel > g_\perp$ so that arguments favoring SP or intermediate geometry over TBP are still valid.

It is important to note that the weighted averages of $a_\perp$ and $a_\parallel$ values as approximated from the frozen-glass spectra do not agree with a_{iso} values obtained from solution measurements on the same complexes. Lack of agreement between measured and theoretical values in pentadentate cobalt(II) systems is well recognized (Niswander, R. H.; Taylor, L. T. *J. Magn. Reson.* **1977**, *26*, 491–503; and our own work with (keto iminato)cobalt(II) complexes, i.e.: Braydich, M. D. M.S. Thesis, Wright State University, Dec 1978). Such inconsistencies have been attributed to significant differences in anisotropy among the compounds and to the fact that a frozen-glass spectrum only approximates single-crystal spectra. The lack of agreement in the Cu(II) parameters is larger than expected, however, and may indicate the presence of Cu(II) complexes of different geometries at the two temperatures or a fluxional mixture of geometric isomers in solution.

I wish to thank Dr. R. D. Bereman for pointing out the inconsistencies in $a_\perp$ and $g_\perp$ values.—Sue C. Cummings