could be related to the amorphous nature of the product.

With $(ClCF_2CO)_2O$ and $(C_3F_7CO)_2O$ the reduced products were mixtures which could possibly contain the chromium(III) fluoroacetate. They were green amorphous solids with no oxidizing power toward acidic KI. Further characterizations of these mixtures were not attempted.

Experimental Section

1. **Chemicals and Equipment.**—The chromium trioxide used was reagent grade. It was dried at 120° *in vacuo* for 4 hr. The anhydrides were dried over P_4O_{10} and distilled prior to use. An infrared spectrum confirmed their purity. The infrared spectra were recorded on a Perkin-Elmer 137 infrared spectrophotometer. The fluorine spectra were obtained with a Varian Model HA-100 analytical nmr spectrometer operating at 94.1 mcps. For the spectrum of $CrO_2(CF_3COO)_2$ with $(CF_3CO)_2O$ in excess and with CCl_3F as an internal standard, the solution composition (by weight) was 23.6% $CrO_2(CF_3COO)_2$, 57.1% $(CF_3CO)_2O$, and 19.3% CCl_3F. For the spectrum of $(CF_3CO)_2O$, with CCl_3F as an internal standard, the solution composition (by weight) was 34.6% CCl_3F and 65.4% $(CF_3CO)_2O$.

X-Ray powder spectra were obtained using an XRD-5 General Electric camera. Nickel-filtered copper radiation (Cu Kα radiation) was used. The procedure was standardized using known compounds (CrO_3, Cr_2O_3, $CrF_3 \cdot 3H_2O$) in which the calculated *d* values agreed with the published ASTM values.

The ultraviolet spectra were recorded using a Cary Model 14 recording ultraviolet spectrophotometer. The samples were dissolved in gas chromatographic spectrophotometric quality CCl_4 (Mallinckrodt). Path length of cells was 1.00 cm.

2. **Chemical Analyses.**—The chromium content was determined iodometrically, after hydrolysis, by quantitatively reducing chromic acid to trivalent chromium. The acidity was determined by titration with a standard base solution using phenophthalein indicator.

3. **Preparation of $CrO_2(CF_3COO)_2$.**—The fused silica reaction vessel ($\sim$100 ml) equipped with a Kontes Teflon stopcock and Teflon stirring bar was evacuated and dried. Chromium trioxide (7.83×10^{-3} mol), previously dried, was added in a drybox and redried *in vacuo*. A slight excess of trifluoroacetic anhydride, 9.54×10^{-3} mol, was vacuum transferred. The vessel was then removed from the liquid nitrogen bath and warmed to room temperature. At room temperature, in the dark, reaction was completed in 5–7 hr. The volatile materials [only $(CF_3CO)_2O$ and traces of COF_2 and CF_3COF] were removed under reduced pressure and the remaining solid was maintained at reduced pressure until it achieved a constant weight. The product [7.40×10^{-3} mol if $CrO_2(CF_3COO)_2$] is a yellow-brown solid (yield *ca.* 95% based on CrO_3); mp 47.5–49.5°; uv (CCl_4) peaks at 286 and 410 mμ. *Anal.* Calcd: Cr, 16.77. Found: Cr, 16.30, 16.25, *via* iodometry; Cr, 16.35, 16.71, *via* acidity (based on eq 2).

4. **Preparation of $Cr(CF_3COO)_3$ from $CrO_2(CF_3COO)_2$.**—To 4.05×10^{-3} mol of CrO_3 in a fused-silica vessel ($\sim$100 ml), a tenfold excess of $(CF_3CO)_2O$ was added. The reactants were heated at $\sim$40° for 5 days. The volatile materials (CO_2, CF_3COF, and COF_2) were removed leaving a green solid whose weight corresponded to 3.96×10^{-3} mol of $Cr(CF_3COO)_3$. *Anal.*[10] Calcd for $Cr(CF_3COO)_3$: C, 18.5; F, 43.7; Cr, 13.3. Found: C, 16.5; F, 40.1; Cr, 16. Some chromium(IV) oxyfluoroacetate was present.

5. **Preparation and Reaction of $CrO_2(ClCF_2COO)_2$.**—The reaction of CrO_3 with $(ClCF_2CO)_2O$ was carried out in essentially the same way as it was with $CrO_2(CF_3COO)_2$. To 1.19×10^{-2} mol of CrO_3, 1.19×10^{-2} mol of $(ClCF_2COO)_2O$ was added. After 7 hr the volatile materials (COF_2, CF_3COF, CrO_2Cl_2) were pumped away until a constant weight loss was achieved. The product [1.05×10^{-2} mol of $CrO_2(ClCF_2COO)_2$] is a yellow-brown solid (yield *ca.* 88% based on CrO_3); mp 64–66°; uv (CCl_4) peaks at 281 and 400 mμ. *Anal.* Calcd: Cr, 15.2. Found: Cr, 14.4, *via* iodometry; Cr, 14.6, *via* acidity.

With excess anhydride (2.7×10^{-2} mol) and CrO_3 (4.9×10^{-3} mol) at 21° for 5 hr and then at 60–70° for 24 hr, a dark green solid was formed (1.442 g, compared to the calculated value for $Cr(ClCF_2COO)_3$ of 1.688 g) along with CrO_2Cl_2, CO_2, and COF_2. The product is not entirely $Cr(ClCF_2COO)_3$; the weight is too low. An infrared spectrum gave the following absorption peaks in cm^{-1}: 1610 (s, b), 1440 (m), 1150 (vs, b) 975 (s), 827 (m), 730 (m). This spectrum is closely analogous to that of $Cr(CF_3COO)_3$. The green solid is slightly soluble in water and soluble in acetone. It is an amorphous solid with no oxidizing power toward acidic KI.

6. **Preparation and Reaction of $CrO_2(CF_3CF_2CF_2COO)_2$.**—To 8.38×10^{-3} mol of CrO_3, 11.9×10^{-3} mol of $(C_3F_7CO)_2O$ was added in a fused-silica reaction vessel. After 4 hr at room temperature the volatile materials (C_3F_7COF, C_2F_5COF, COF_2, and CO_2) were pumped away at 0° leaving a brown solid [8.16×10^{-3} mol of $CrO_2(C_3F_7COO)_2$] (yield *ca.* 97% based on CrO_3); uv (CCl_4) peaks at $\sim$380 and 278 mμ. The solid was unstable and could not be handled further at room temperature without decomposition. Analysis of hydrolyzed samples gave satisfactory but tentative results. *Anal.* Calcd: Cr, 10.2. Found: Cr, 10.3, *via* iodometry; Cr, 10.5, *via* acidity. With excess $(C_3F_7CO)_2O$ at 90° for 17 hr a green amorphous product [whose weight corresponded to the empirical composition $Cr(C_{3.2}F_{5.4}O_2)_3$] was formed. The structure of this solid is unknown.

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Cyanatopentaamminecobalt(III). Preparation from Urea and Kinetics of Acid-Catalyzed Decomposition

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Linhard and Flygare[1] found that the reaction of NCO^- with $(NH_3)_5CoOH_2^{3+}$ gave the carbamato complex $(NH_3)_5CoO_2CNH_2^{2+}$ as product. In a more recent study Sargeson and Taube[2] have confirmed this result and have shown that the reaction occurs without cleavage of the Co–O bond in $(NH_3)_5CoOH_2^{3+}$. Ablov, Popova, and Samus[3] have reported the dimethylglyoxime (DMG)–cobalt(III) complexes $(DMG)_2Co(NCO)(OH_2)$ and $(DMG)_2Co(NCO)_2^-$. These were observed to hydrolyze in aqueous acid to give $(DMG)_2Co(NH_3)(OH_2)^+$ and $(DMG)_2Co(NH_3)_2^+$.

This note reports the preparation of N-bonded

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[1] M. Linhard and H. Flygare, *Z. Anorg. Allgem. Chem.*, **251**, 25 (1943).

[2] A. M. Sargeson and H. Taube, *Inorg. Chem.*, **5**, 1094 (1966).

[3] A. V. Ablov, A. A. Popova, and N. M. Samus, *Zh. Neorgan. Khim.*, **14**, 994 (1969); *Chem. Abstr.*, **7**, 18421 (1969).

cyanatopentaamminecobalt(III) by the reaction of $(NH_3)_5CoOH_2^{3+}$ with urea, several N-substituted ureas, and urethane. Evidence is presented that the reaction proceeds through an N-bonded urea complex which decomposes to $(NH_3)_5CoNCO^{2+}$ and NH_4^+. The O-bonded urea complex has also been prepared and characterized.

$(NH_3)_5CoNCO^{2+}$ decomposes in acid solution to give $Co(NH_3)_6^{3+}$ and CO_2. The kinetics of this reaction are also reported here.

Experimental Section

A. Preparation of $((NH_3)_5CoNCO)(ClO_4)_2$.—(1) A 10-g sample of $((NH_3)_5CoOH_2)(ClO_4)_3$ and 10 g of either urea or methylurea or phenylurea were dissolved in 80 ml of trimethyl phosphate over ~5 g of Linde molecular sieves. The mixture was heated on the steam bath for 1 hr during which time the solution changed from orangish red to reddish purple. The solution was cooled and the product was precipitated by the addition of *sec*-butyl alcohol (~500 ml). The product was collected by filtration and recrystallized from warm water (40–50°) containing a small amount of $NaClO_4$.

The product is a red crystalline compound. The visible spectrum shows peaks at 501 nm (ϵ 130) and 353 nm (ϵ 84.8). The discussion gives data on the infrared and nmr spectra.

(2) A 10-g sample of $((NH_3)_5CoOH_2)(ClO_4)_3$ was dissolved in molten urea (~50 g) at 135–136° and stirred for 3 hr in the presence of 5 g of molecular sieves. The reaction mixture was cooled and the urea was extracted with *sec*-butyl alcohol. The product was collected by filtration and recrystallized four times from dilute aqueous sodium perchlorate. The resulting complex had the same properties as that from section A1 except that the extinction coefficients indicated that a small amount of $Co(NH_3)_6^{3+}$ was present.

(3) A 3-g sample of $((NH_3)_5CoOP(OCH_3)_3)(BF_4)_3$[4] was dissolved in molten urethane (~30 g) (~65°) and stirred for 5 hr, in the presence of 1 g of molecular sieves. Then the urethane was extracted into 98% ethanol (200 ml) and the complex was filtered off. The crude product was recrystallized as in section A1 and gave a product having properties identical with those of the product from section A1.

It is claimed by Fraser[5] that a preparation similar to this produces the N-bonded urethane complex. Attempts to repeat Fraser's method, which starts with $((NH_3)_5CoOH_2)(NO_3)_3$, have yielded $((NH_3)_5CoNO_3)(NO_3)_2$, starting material, and cobalt(II) species depending on the reaction time.

B. Preparation of $((NH_3)_5CoOC(NH_2)_2)(ClO_4)_3$.—(1) A 12-g sample of $((NH_3)_5CoOH_2)(ClO_4)_3$ and 15 g of urea were dissolved in 100 ml of N,N-dimethylacetamide over 5 g of molecular sieves. The mixture was heated on a steam bath for 1 hr and the crude product was isolated using *sec*-butyl alcohol as described in section A1. Fractional crystallization from warm water containing $NaClO_4$ yielded two complexes, the cyanato compound and the O-bonded urea compound. The perchlorate salt of the latter is much more soluble in water.

The visible spectrum of the urea complex shows maxima at 514 nm (ϵ 78.9) and 350 nm (ϵ 60.3). The infrared spectrum shows the characteristic urea pattern[6] in the 3000–3500- and 1550–1650-cm^{-1} regions; the strongest peak in the former is at 3300 cm^{-1} and in the latter is at 1640 cm^{-1}. The frequency shifts from free urea are consistent with the presence of O-bonded urea in the cobalt complex.[6]

The nmr spectrum in DMSO-d_6 shows the three *trans* NH_3 protons at τ ~7.5 (partly hidden by the solvent peak), the twelve *cis* NH_3 protons at τ 6.12, and the four urea NH_2 protons at τ 3.38.

(2) When the preparative procedure A1 was followed using carbanilide ($(C_6H_5NH)_2CO$) or tetramethylurea, no cyanato product was obtained. The products from these two reactants were unreacted $((NH_3)_5CoOH_2)(ClO_4)_3$ and some dimethylphosphato complex. The latter may arise from solvent decomposition during the reaction or may be an impurity in the solvent.

Analysis of Complexes.—Very similar analyses were obtained for $((NH_3)_5CoNCO)(ClO_4)_2$ obtained from methods A1, A3, and B1. A typical analysis is given. *Anal.* Calcd: C, 3.12; H, 3.90; N, 21.8. Found: C, 3.23; H, 4.02; N, 21.7. Found from method A2: C, 3.19; H, 4.08; N, 22.8. *Anal.* from method B1. Calcd for $((NH_3)_5CoOC(NH_2)_2)(ClO_4)_3$: C, 2.39; H, 3.79; N, 19.5. Found: C, 2.39; H, 3.74; N, 19.2.

The visible spectra and extinction coefficients were determined with a Cary 14 spectrophotometer. Nmr spectra were recorded at 40° on a Varian A56-60 spectrometer. Infrared spectra were measured using a Perkin-Elmer 421 grating spectrometer using potassium bromide disks or Nujol mulls.

Kinetic Procedure.—Preliminary qualitative observations indicated that $(NH_3)_5CoNCO^{2+}$ decomposed to $Co(NH_3)_6^{3+}$ and CO_2 in acidic solution. The $Co(NH_3)_6^{3+}$ product was identified by comparison of the visible, infrared, and nmr spectra to those of an authentic sample and also by C–H–N analysis.

The rate of the reaction was studied by following the change in absorbance at 500 nm on a Bausch and Lomb Precision spectrophotometer. The rate was studied as a function of $[H^+]$ and temperature in a $LiClO_4$–$HClO_4$–H_2O medium at constant ionic strength of 1.0 *M*. Rate constants were obtained from the usual logarithmic plots of absorbance at time *t*, minus the absorbance after complete reaction. Some difficulty was encountered at 5° due to the insolubility of $Co(NH_3)_6(ClO_4)_3$ but the logarithmic plots were generally linear for greater than 85% of the reaction.

Reagent grade lithium perchlorate (G. F. Smith Chemical Co.) and perchloric acid (Baker and Adamson) were used as supplied. The lithium perchlorate solution was standardized by determining the amount of $[H^+]$ released from a Dowex 50-X8 ion-exchange column. The temperature was controlled using a Colora constant-temperature bath (in conjunction with a Rho circulating cooler for temperatures below 20°) and a Thermistemp temperature controller (Model 71) with the thermistor probe in the cell holder of the spectrophotometer.

Results and Discussion

A number of publications have appeared recently on the preparation and bonding mode of cyanate, selenocyanate, and thiocyanate ions in various complexes.[7] The cyanate ion appears to be bonded to the metal ion through nitrogen in all its complexes except possibly for $Re(OCN)_6^{2-}$, $Re(OCN)_6^{-}$, $Mo(OCN)_6^{3-}$,[8] and $(C_5H_5)_2Ti(OCN)_2$.[9] All of the chemical and spectral data for $(NH_3)_5CoNCO^{2+}$ indicate that the cyanate ion is bonded through nitrogen.

The chemical evidence provides the strongest support for nitrogen bonding of cyanate. In acid solution the complex decomposes *via* the reaction

$$(NH_3)_5CoNCO^{2+} + H_3O^+ \longrightarrow Co(NH_3)_6^{3+} + CO_2 \qquad (1)$$

If the complex were oxygen bonded, the product would be $(NH_3)_5CoOH_2^{3+}$.

The infrared spectrum of the complex is also consis-

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[4] This compound was prepared by heating $((NH_3)_5CoOH_2)(BF_4)_3$ (I) in trimethyl phosphate, over molecular sieves, for 1 hr on a steam bath. The product was precipitated by adding ether and *sec*-butyl alcohol and was used without further purification. I was prepared by addition of 50% HBF_4 to an aqueous solution of the corresponding perchlorate salt and recrystallized twice from dilute aqueous HBF_4.

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[6] R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 1575 (1957).

[7] J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968).

[8] R. A. Bailey and S. L. Kozak, *J. Inorg. Nucl. Chem.*, **31**, 689 (1969).

[9] J. L. Burmeister, E. A. Deardorff, and C. E. Van Dyke, *Inorg. Chem.*, **8**, 170 (1969).

TABLE I

INFRARED STRETCHING FREQUENCIES FOR COORDINATED CYANATE

Compound	ν_1(C–O), cm^{-1}	ν_3(C–N), cm^{-1}	Ref
$[Pd(Et_4dien)NCO][B(C_6H_5)_4]$	1335	2220	10
$[Pd(dien)NCO][B(C_6H_5)_4]$	1329	2222	10
$[(NH_3)_5CoNCO][ClO_4]_2$	1335^a	2265	This work
KNCO	1254^b	2158	10

^{a} The deuterated complex was used to assign ν_1 because the symmetric NH_3 deformation interferes in this region. ^{b} A doublet due to Fermi resonance of bending and C–O stretching modes is observed. The value cited is for the unperturbed C–O stretching frequency.

tent with that of other known[10] N-bonded cyanate complexes (Table I). The C–O and C–N stretching bands appear at higher frequencies than those in an ionic cyanate (KNCO).

The nmr spectrum of $((NH_3)_5CoNCO)(ClO_4)_2$ in DMSO-d_6 gives the chemical shift of the twelve protons on *cis* NH_3 ligands at τ 6.58 and three protons on the *trans* NH_3 at τ 7.08 (relative to DMSO protons at τ 7.48). The chemical shift of the *trans* NH_3 protons is consistent with an N-bonded complex as discussed in a previous paper.[11] In addition, it has been noted that the chemical shift difference between the *cis* and *trans* NH_3 protons is characteristic of the coordinating atom in various $Co(NH_3)_5$-type complexes. For O-bonded ligands the *trans* minus *cis* chemical shift difference is 1.0–1.5 τ units, for N-bonded compounds 0–0.6 τ unit, and for C-bonded compounds $((NH_3)_5CoCN^{2+})$ ~ -1.0 τ unit.[12] Nitrogen bonding in the cyanate complex is consistent with this correlation.

The kinetics of reaction 1 have been studied at 5.0, 15.0, and 25.0° in 0.021–0.217 *M* $HClO_4$, at an ionic strength of 1.0 *M*, adjusted with $LiClO_4$. The results are given in Table II. The rate of disappearance is given by

$$-\frac{d \ln [(NH_3)_5CoNCO^{2+}]}{dt} = k_0 = k_1[H^+] \qquad (2)$$

The rate constant k_1 was determined at each temperature from the slope of a plot of k_0 *vs.* $[H^+]$. The values of k_1, $\Delta H_1^{\ddagger}$, and $\Delta S_1^{\ddagger}$ are given in Table III.

TABLE II

HYDROLYSIS OF $(NH_3)_5CoNCO^{2+}$ IN ACID SOLUTION AT μ = 1.0 ($LiClO_4$)

Temp, °C	$[HClO_4]$, *M*	10^3k_0, sec^{-1} Obsd	Calcd
5.0	0.087	2.47	2.52
	0.174	4.88	5.04
	0.217	6.60	6.29
15.0	0.052	3.98	4.06
	0.070	5.46	5.46
	0.087	6.60	6.59
	0.122	9.63	9.52
	0.174	13.1	13.6
25.0	0.021	3.27	3.40
	0.035	5.50	5.67
	0.052	8.80	8.42
	0.070	11.2	11.3
	0.087	14.4	14.1

TABLE III

KINETIC PARAMETERS FOR ACID HYDROLYSIS OF $(NH_3)_5CoNCO^{2+}$

Temp, °C	k_1, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal mole^{-1}	$\Delta S^{\ddagger}$, eu
5.0	0.029 ± 0.001		
15.0	0.078 ± 0.001		
25.0	0.162 ± 0.002	13.1 ± 0.5	−18 ± 2

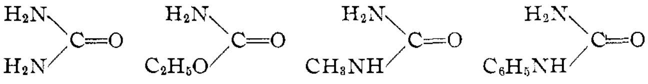
Jensen[13] has studied the kinetics of decomposition of cyanic acid and found for the reaction

$$OCNH + H_3O^+ \longrightarrow NH_4^+ + CO_2 \qquad (3)$$

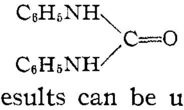
a rate constant of 1.2 M^{-1} sec^{-1} at 25° (obtained by extrapolation) and $\Delta H^{\ddagger}$ of 15.1 kcal mol^{-1}. These results are in good agreement with the previous work of Lister.[14] The kinetic parameters for $(NH_3)_5CoNCO^{2+}$ are rather similar indicating that $(NH_3)_5Co^{3+}$ in the complex has a similar role to the hydrogen in HNCO.

The most unusual aspect of this work is the conversion of urea and several urea derivatives to the nitrogen-bonded cyanate ligand. The original goal of our work was to prepare the O-bonded urea compound in order to test previous proposals concerning electron-transfer reactions.[9] It seemed likely that this would be rather simple in view of the large number of urea complexes which have already been prepared. This expectation was not borne out, however, and every preparation seemed to give the cyanato complex as a major product. The existence of the latter is not surprising,[3] and it could probably be made more directly from a cyanate salt and either $(NH_3)_5CoOP(OCH_3)_3^{3+}$ or $(NH_3)_5CoN_3^{2+}$ + $NOClO_4$ in a poorly coordinating solvent such as trimethyl phosphate. However production of the cyanato complex from urea was quite unexpected.

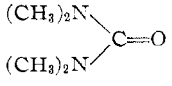
In order to explore the generality of this reaction and perhaps learn something of the reaction pathway, several urea derivatives have also been used as starting materials. The following were found to yield the cyanato complex as a product, using preparative methods A1 and A2



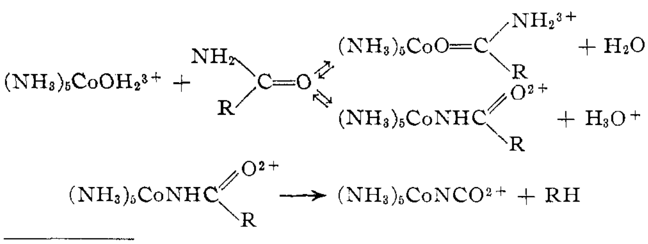
However, under similar conditions no cyanate complex was obtained from



or



These results can be understood most easily in terms of the reactions



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(10) J. L. Burmeister and N. J. Stefano, *Inorg. Chem.*, **8**, 1546 (1969).

(11) R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, **92**, 1533 (1970).

(12) J. A. Stanko and T. W. Starinshak, *Inorg. Chem.*, **8**, 2156 (1969). The spectrum of $(NH_3)_5RuCO^{2+}$ gives a difference of −1.0 τ unit where the bonding is also through carbon indicating that the nmr correlation may also prove useful for ruthenium(II) complexes.

(13) M. B. Jensen, *Acta Chem. Scand.*, **12**, 1657 (1958).

(14) M. W. Lister, *Can. J. Chem.*, **33**, 426 (1955).

where R = NH_2, NHCH, NHC_6H_5, or OC_2H_5. Carbanilide and tetramethylurea may not produce the cyanato complex either because steric interactions make formation of the N-bonded complex very unfavorable or because it would be necessary for phenyl or methyl groups to migrate. The fact that the O-bonded isomer of urea has been isolated and does not seem to isomerize in solution or in the solid state indicates that O- to N-linkage isomerism is more likely to proceed by dissociation, as implied in the above reaction scheme, and not by intramolecular rearrangement.

The reactions outlined above may provide a model for metal ion catalyzed decomposition of urea. The crucial feature is the formation of the N-bonded urea complex which then forms the conjugate base of urea because the metal ion greatly increases the acidity of the coordinated $-NH_2$ protons.[15] The conjugate base of urea then easily decomposes to cyanate and ammonia.

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[15] L. L. Po and R. B. Jordan, *Inorg. Chem.*, **7**, 526 (1968).

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Electron Spin Resonance Spectra of Transition Metal Ions in Oxidation–Reduction Systems

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When solutions of $TiCl_3$ and H_2O_2 were mixed in an esr cavity, Dixon and Norman[3] observed a narrow singlet spectrum, line width 1 G, which they attributed to the ·OH radical. Other workers[4-15] have reported similar esr spectra for this system. Also, for this system an esr spectrum with two narrow lines, spaced a few gauss apart, has been reported[8,11,13] These lines have been assigned (1) to ·OH radicals and ·OOH radicals complexed with Ti^{4+} ions,[8] (2) to ·OOH radicals and ·OH or ·OOH radicals associated with titanium,[11] and (3) to ·OH radicals and ·OH radicals complexed with Ti^{4+} ions.[13]

When, in a similar manner, H_2O_2 and Ce^{4+}, Fe^{2+}, or Fe^{3+} ions were mixed in an esr cavity, no esr spectra with narrow line widths were observed, although the formation of ·OH and ·OOH radicals should occur. However, when Ti^{4+} ions were added to the Ce^{4+}–H_2O_2, Fe^{2+}–H_2O_2, and Fe^{3+}–H_2O_2 systems, esr spectra similar to that generated by the Ti^{3+}–H_2O_2 system[3] were observed.[4,6] The intensity of the signal was dependent on and proportional to the concentration of Ti^{4+} ions added. This dependence indicated that there was a greater concentration of free radicals formed in the systems than was being detected by esr spectroscopy. If Ti^{4+} ions were not added to the systems, esr spectra with line widths of about 1 G were not observed for these systems.[6] Oxyvanadium (V) ions also interacted with free radicals, formed in these systems, to generate esr spectra.[5]

We have observed that when transition metal ions, such as ZrO^{2+}, Hf^{4+}, Th^{4+}, and UO_2^{2+} ions, were added to these oxidation–reduction systems, esr spectra, similar to those generated when Ti^{4+} ions were added to these systems, were recorded.[4,6] The *g* values and line widths for the esr spectra generated in oxidation–reduction systems containing certain transition metal ions are shown in Table I. With Hf^{4+} ions, changing the experimental conditions did not alter the relative intensities of the two absorption bands which probably indicated that some hyperfine interaction split the line. The addition of $Ce_2(SO_4)_3$, $La(NO_3)_3$, H_2MoO_4, $(NH_4)_2MoO_4$, $NbCl_5$, $ScCl_3$, $TaCl_5$, H_2WO_4, or YCl_3 to these oxidation–reduction systems did not result in the formation of any complexes with the free radical species in these systems which generated esr spectra.

TABLE I

LINE WIDTHS AND *g* VALUES OF THE HYPERFINE COMPONENTS OF THE ESR SPECTRA GENERATED BY OXIDATION–REDUCTION SYSTEMS CONTAINING TRANSITION METAL IONS AT 22°

Metal ion	*g* value	Line width, G	Metal ion	*g* value	Line width, G
Ti^{4+}	2.0129[a]	0.95	Hf^{4+}	2.0141[b]	1.20
Ti^{4+}	2.0115[b]	0.75	Th^{4+}	2.0177	1.25
ZrO^{2+}	2.0141	2.10	UO_2^{2+}	2.0217	1.50
Hf^{4+}	2.0154[a]	1.30			

[a] Low field. [b] High field.

From these data, it would appear that some transition metal ions in their highest stable oxidation state form complexes with the free-radical species in oxidation–reduction systems to generate characteristic esr spectra. The Sc group of metals do not form stable peroxy compounds, so that any complexes formed by these metals with the free radical species in the

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