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Facile Syntheses and Characterization of Pentaamminechromium(III) Complexes with Neutral O- and N-bound Ligands

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Abstract

The ready substitution of coordinated trifluoromethanesulfonate on pentaamminechromium(III) has been applied to the facile synthesis of a range of complexes of neutral ligands, $[Cr(NH_3)_5(L)]^{3+}$ (L = OH_2, $OHCH_3$, $OS(CH_3)_2$, $OP(OCH_3)_3$, $OC(NH_2)_2$, $OC(NHCH_3)_2$, $OC(CH_3){\cdot}N(CH_3)_2$, $OCH{\cdot}NH_2$, $OCH{\cdot}N(CH_3)_2$, $NCCH_3$, NH_3 and imidazole). The complexes have been characterized by microanalysis, electronic and infrared spectroscopy, and the lability of the neutral ligand towards acid hydrolysis determined, and compared with cobalt(III) analogues.

Introduction

The chemistry of the inert d^3 metal ion chromium(III) has been well studied, but is less extensive than that of inert d^6 cobalt(III) [1]. Comparisons of these two readily accessible first-row metal ions has indicated that the mechanisms of their reactions as amine complexes may differ. Associative pathways may exist for hydrolysis of chromium(III) complexes, while cobalt(III) complexes undergo reaction by dominantly dissociative pathways [2, 3]. In studying the basic mechanisms of reactions of these ions, the pentaammine complexes offer the simplest systems for study. Recently, the syntheses of pentaammine complexes of coordinated trifluoromethanesulfonate ($^-OSO_2CF_3$) for several metal ions has provided possible facile routes to a range of complexed ligands not previously readily accessible [4–6]. Particularly for chromium(III), where ammine ligands are far more labile than is the case for cobalt(III), vigorous synthetic conditions will lead to decomposition. From the labile $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ precursor, however, facile, mild and rapid substitution reactions to produce in high yield a range of complexes can be developed, and are described here.

Experimental

Syntheses

Dried and/or distilled solvents and recrystallized ligands were employed routinely. $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ was prepared as previously described [6], and was isolated as an analytically pure pink powder. **CAUTION.** Metal perchlorates represent a potential explosive hazard. While no problems were experienced in these syntheses, due care must be exercised.

Pentaammine(trimethylphosphate)chromium(III) Perchlorate Monohydrate

A solution of $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2.0 g) in trimethylphosphate (20 ml) was stirred at room temperature for 2 h. The crude product was isolated by addition of ethanol (20 ml) then ether (200 ml), with stirring, and collected by filtration on a fine porosity glass frit. The solid was redissolved in ethanol (15 ml) and a solution of $LiClO_4$ (2.5 g) in ethanol (10 ml) added immediately. Fluffy pink crystals appeared rapidly. These were collected, washed with 1:1 ethanol:ether, then ether, and air dried (0.86 g, 50%). *Anal.* Calcd. for $C_3H_{26}N_5Cl_3CrO_{17}P$: C, 6.07; H, 4.42; N, 11.80; P, 5.22. Found: C, 6.2; H, 4.3; N, 11.55; P, 5.2.

Pentaammine(dimethylsulfoxide)chromium(III) Perchlorate Monohydrate

A solution of $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2.0 g) in dimethylsulfoxide (20 ml) was reacted and the crude product isolated as described above. The crude product was dissolved in water (20 ml) and 70% $HClO_4$ (5 ml) added slowly. Pink needles formed readily on cooling, and were collected, washed with ethanol, then ether, and air dried (1.4 g, 80%).

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Anal. Calcd. for $C_2H_{23}N_5Cl_3CrO_{14}S$: C, 4.52; H, 4.36; N, 13.17. Found: C, 4.5; H, 4.3; N, 13.1.

Pentaammine(dimethylacetamide)chromium(III) Perchlorate Monohydrate

A solution of $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2.0 g) in N,N-dimethylacetamide (20 ml) was reacted and the crude product isolated as described above. The product was dissolved in water (10 ml) by slight warming, and a solution of $NaClO_4$ (2 g) in water (10 ml) added. Upon cooling in ice, a pink precipitate was obtained and collected. A second crop was obtained by addition of ethanol to the filtrate. Both fractions were combined and dissolved in warm water (5 ml) and $LiClO_4$ (2 g) in ethanol (5 ml) added immediately. Pnik crystals formed rapidly upon cooling and were collected, washed with ethanol and ether and air dried (0.87 g, 50%). *Anal.* Calcd. for $C_4H_{26}N_6Cl_3CrO_{14}$: C, 8.89; H, 4.85; N, 15.54. Found: C, 8.6; H, 4.5; N, 15.6.

Pentaammine(formamide)chromium(III) Trifluoromethanesulfonate Diperchlorate

This compound was prepared from $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (1.0 g) as described previously [7], except the crude product was recrystallized from water (5 ml) by addition of $NaClO_4$ (2 g) and $NaOSO_2CF_3$ (2 g) in water (4 ml) and cooling. Orange plates were collected, washed with ethanol and air dried (0.60 g, 57). *Anal.* Calcd. for $C_2H_{18}N_6Cl_2CrF_3O_{12}S$: C, 4.53; H, 3.42; N, 15.85; S, 6.05. Found: C, 4.6; H, 3.6; N, 15.7; S, 6.5.

Pentaammine(acetonitrile)chromium(III) Trifluoromethanesulfonate Monohydrate

A solution of $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2.34 g) in acetonitrile (10 ml) was refluxed for 15 min. The solution was filtered, and orange crystals formed upon cooling in an ice-bath. These were collected, washed with diethyl ether, and air dried (2.0 g, 80%). *Anal.* Calcd. for $C_5H_{20}N_6CrF_9O_{10}S_3$: C, 9.33; H, 3.13; N, 13.06. Found: C, 9.4; H, 3.0; N, 13.0.

Pentaammine(imidazole)chromium(III) Perchlorate Monohydrate

A solution of $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2.0 g) and imidazole (2.0 g) in sulfolane (20 ml) was stirred and heated for 10 min. Addition of ethanol (20 ml) and ether (200 ml) separated a yellow oil. The solvent was decanted, and the oil dissolved in ethanol (20 ml). Slow addition of ether precipitated a yellow solid, which was collected on a sintered frit and air dried. The powder was dissolved in water (10 ml) and concentrated $HClO_4$ (4 ml) added slowly to precipitate the complex. This solid may be recrystallized further by dissolution in water (5 ml) with warming, followed by concentrated $HClO_4$ addition to the first sign of permanent cloudiness (~1 ml). Further addition of concentrated $HClO_4$ (1 ml) and cooling in an ice-bath yielded yellow needles which were collected, washed with ethanol and ether and air dried (0.58 g, 35%). *Anal.* Calcd. for $C_3H_{21}N_7Cl_3CrO_{13}$: C, 6.91; H, 4.06; N, 18.80. Found: C, 6.5; H, 3.7; N, 18.7.

Pentaammine(methanol)chromium(III) Trifluoromethanesulfonate

Magnesium-dried methanol (20 ml) was distilled onto $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2 g) and the solution stirred under N_2 for 2 h. The solvent was removed on a vacuum line to give a quantitative yield of red powder. The product is moisture sensitive, and should be stored in a dessicator. *Anal.* Calcd. for $C_4H_{19}N_5CrF_9O_{10}S_3$: C, 7.79; H, 3.11; N, 11.35. Found: C, 7.6; H, 3.1; N, 10.7.

Pentaammine(dimethylformamide)chromium(III) Perchlorate Monohydrate

This was prepared from $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ exactly as described [7]. *Anal.* Calcd. for $C_3H_{25}N_6Cl_3CrO_{13}$: C, 6.84; H, 4.59; N, 15.96. Found: C, 7.1; H, 4.4; N, 15.8.

Pentaamine(urea)chromium(III) Dithionate Dihydrate

This was prepared from $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ exactly as described [7]. *Anal.* Calcd. for $CH_{23}N_7CrO_{12}S_3$: C, 2.54; H, 4.70; N, 20.71. Found: C, 2.6; H, 4.8; N, 21.1.

Pentaammine(N,N'-dimethylurea)chromium(III) Dithionate Sesquihydrate

This was prepared from $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ as described [7]. *Anal.* Calcd. for $C_3H_{26}N_7CrO_{11\frac{1}{2}}S_3$: C, 7.31; H, 5.32; N, 19.91. Found: C, 7.0; H, 5.2; N, 19.9.

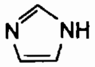
Hexaamminechromium(III) Perchlorate Monohydrate

A solution of $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (2.0 g) in liquid ammonia (~10 ml) was allowed to evaporate to dryness. The yellow solid was dissolved in water (10 ml) and concentrated $HClO_4$ (4 ml) added. After cooling in an ice-bath, the yellow solid was collected, washed with ethanol and ether, and air dried (1.1 g, 75%). *Anal.* Calcd. for $H_{20}N_6Cl_3CrO_{13}$: H, 4.38; N, 17.86. Found: H, 4.0; N, 17.9.

Pentaammine(aqua)chromium(III) ion

It may be prepared in quantitative yield from aquation of the trifluoromethanesulfonato precursor, and may be recrystallized and isolated as the perchlorate salt if required [6].

TABLE I. Electronic Spectra of Pentaamminechromium(III) Complexes.

Ligand	λ, nm (ε, M^{-1} cm^{-1})	Ligand	λ, nm (ε, M^{-1} cm^{-1})
OH_2	480(37); 360(32)	$OC(NH_2)_2$	504(58); 370(38)
$OHCH_3$	490(33); 363(29)	$OC(NHCH_3)_2$	506(63); 374(39)
$OS(CH_3)_2$	496(41); 369(33)	$OP(OCH_3)_3$	496(39); 365(30)
$OC(CH_3)\cdot N(CH_3)_2$	504(61); 368(38)	$NCCH_3$	468(35); 351(34)
$OCH\cdot NH_2$	488(51); 362(35)	NH_3	463(47); 350(34)
$OCH\cdot N(CH_3)_2$	488(48); 365(35)		466(41); 353(35)

Pentaammine(dimethylacetamide)cobalt(III) Trifluoromethanesulfonate Hydrate

A solution of $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (1.0 g) [4] in dry dimethylacetamide (10 ml) was stirred at room temperature for 1 hr, and the product precipitated by the addition of ethanol (10 ml) and ether (200 ml). The resultant red powder was dissolved in water (5 ml) at room temperature and carmine red flakes of the product were precipitated by the addition of $NaOSO_2CF_3$ (1 g) to the stirred solution (1.6 g, 70%). *Anal.* Calcd. for $C_7H_{26}N_6CoF_9S_9O_{11}$: C, 12.07; H, 3.76; N, 12.07. Found: C, 12.3; H, 3.8; N, 12.0. The synthesis of this cobalt(III) complex has not been described previously; its synthesis was performed for comparison with the chromium(III) analogue, employing the standard method [4].

Physical Methods

Absorption spectra were recorded using a Hewlett-Packard 8450A spectrophotometer. Infrared spectra were recorded as KBr discs on a Nicolet MX-1 FT-IR spectrometer. Aquation rates in 0.01 M $HClO_4$ were determined using a Hitachi 220A spectrophotometer.

Results and Discussion

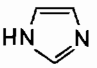
The trifluoromethanesulfonatopentaamminechromium(III) ion has a labile $CF_3SO_3^-$ (k_{aq} 0.012 s^{-1}, 25 °C, 0.01 M CF_3SO_3H), which can be displaced by other potential ligands apart from water. We have established ready substitution by a range of coordinating solvents (water, methanol, acetonitrile, dimethylsulfoxide, trimethylphosphate, dimethylacetamide, formamide, dimethylformamide and ammonia) or by coordinating solid ligands (urea and imidazole) in a poorly coordinating solvent such as sulfolane. Reactions proceed very rapidly under mild conditions. Reactions to the trifluoromethanesulfonate salts are essentially quantitative, with final yields after recrystallization high. The reactions described should be applicable to other chromium(III) amines.

The complexes of imidazole, trimethylphosphate, methanol and dimethylacetamide have not been reported previously, while those of urea, acetonitrile and formamide have only been reported recently, prepared from the same trifluoromethanesulfonato route [6, 7]. While alternative routes to other complexes have been reported [8–10], these are less facile or lower yielding. Unlike cobalt(III) ammines, where extreme conditions may be applied if necessary in syntheses due to the inertness of coordinated ammonia, chromium(III) amines are susceptible to hydrolysis and substitution. For example, the first synthesis of ureapentaamminecobalt(III) employed quite severe conditions [11], which could not be extended readily to the chromium(III) analogue. The rate constant for aquation of hexaamminechromium(III) (1.7×10^{-7} s^{-1} at 25 °C) [12] is about 10^5 faster than that of hexaamminecobalt(III) (5.8×10^{-12} s^{-1} at 25 °C) [13], for example. The greater lability of ammonia on chromium(III) also required synthesis of the trifluoromethanesulfonato precursor at room temperature rather than the elevated temperatures appropriate for cobalt(III) [6].

The electronic spectra of the pentaamminechromium(III) complexes in the visible region show the two characteristic bands of chromium(III) arising from $^4B_{1g} \rightarrow {}^4T_{2g}(O_h)$ and $^4B_{1g} \rightarrow {}^4T_{1g}(O_h)$ transitions. For urea, N,N′-dimethylurea and formamide both O-bound and N-bound isomers are possible, but only the O-bound isomer is prepared under the reaction conditions employed [7]. The electronic spectra of these complexes are consistent with this since these and other O-bound ligand complexes all exhibit the lowest-energy maxima at lower energy than the maximum of the aqua complex. Maxima for the N-donor ligands are invariably at higher energy. Maxima are collected in Table I.

Apart from microanalysis and electronic spectroscopy, clear evidence for incorporation of the neutral ligands into the complex coordination sphere comes from the infrared spectroscopy (Table II). Strong absorbances from coordinated ammines are observed in the usual positions (near 3210, 1615, 1310 and 770 cm^{-1}) with little variation. Characteristic perchlorate bands occur at 1070–1145 cm^{-1} and near

TABLE II. Infrared Spectra of Pentaamminechromium(III) Complexes.

Ligand	Infrared Absorbances (cm^{-1})[a]
NH_3	3450s,sh 3210vs 1612s 1312s 1140–1075vs,br 744s 636s 626s 466w 352w 323w
OH_2	3400s,sh 3190vs 1615s 1310s 1145–1080vs,br 752s 634s 624s 480w 350w
$OHCH_3$	3530s,br 3250vs,br 2875w 2846w 1624s 1255vs,br 1174vs 1030s 994m 765s 632s 580m 522m 470w 353w 322w
$OC(CH_3)\cdot N(CH_3)_2$	3450s,br 3200vs,br 2950w,sh 1630s,sh 1615s, 1507s 1425m 1410m 1365w 1313s 1262w 1145–1075vs,br 977w 782s 638s 629s 464m 350w
$OCH\cdot N(CH_3)_2$	3500s,br 3210vs,br 2937w,sh 1660s 1615s 1496w 1435m 1419w 1381s 1310m 1296m 1252w 1145–1075vs,br 785s 713m 635s 624s 468m 443w 395m 357w 320w
$OP(OCH_3)_3$	3430s,br 3210vs,br 2966w 2856w 1617s 1456m 1310s 1212s 1145–1070vs,br 1040s,sh 878m 870m 857w 787s 636s 626s 543w 515w 493w 469m 358w 325w
$OC(NH_2)_2$	3520s 3320s 3200vs,br 1636s 1568s 1497m 1330m 1305s 1240vs,br 1160m,sh 1035w 992s 767s 588s 560s,sh 515s 470m 385w 360w 323w
$OCH\cdot NH_2$	3530s 3440s 3210vs,br 1685s 1619s 1556m,sh 1375s 1315s 1280s,br 1250s,sh 1140–1070vs, br 1036s 772s 730m,sh 638s,sh 630s 580w 521m 478w,sh 463m 355w 325w
$OS(CH_3)_2$	3460s,br 3210vs,br 2960w,sh, 2913w 1618s 1419m 1407m 1325s 1297s 1145–1070vs,br 983s 956s 770s 636s 626s 488m 465m 350vw 329w
	3420s,br 3210vs,br 2960w 2886w 1617s 1550m 1518m 1444w 1421w 1401w 1312s 1140–1075vs,br 955w 774s 757s 728m,sh 638s 627s 480w,sh 468m 350w
$NCCH_3$	3520s,br 3220vs,br 2334m 2304w 1625s 1318s 1255s,br 1170s 1032s 963w 787s 766s,sh 645s 633s 581m 523m 472m 424w 354w 320w
$OC(NHCH_3)_2$	3500s,sh 3240vs 2940w,sh 1608s 1490w,sh 1442m 1402m 1358m 1305s 1242vs,br 1175m,sh 1091w 1050w 992s 910w, 780s 660w 584s 570s 515s 465m 385w 352w 320w

[a] KBr discs; s strong; m medium; w weak; v very; br broad; sh shoulder.

630 cm^{-1}. Dithionate anion in the urea complexes can be assigned absorbances observed near 1240, 990, 770, 580 and 515 cm^{-1}. Trifluoromethanesulfonate anion exhibits characteristic bands near 1250, 1170, 635, 580, 520, 355 and 320 cm^{-1}; the IR absorbances of this anion have been assigned completely for the Ag^+ salt [14]. The bands assignable to the sixth ligand approximate but do not necessarily coincide with the bands for the free ligands [15]. A weak to medium absorbance near 465 cm^{-1} in each ion may be assigned to the ν(Cr–N), in agreement with earlier assignment [16], while weak absorbances near 350 cm^{-1} and 320 cm^{-1}, hidden by bands from $CF_3SO_3^-$ in some complexes, may be associated with δ(N–Cr–N), although these latter assignments are tenuous. Shifts in frequencies of the coordinated ligands compared with the free ligands are a general phenomenon particularly for vibrations involving the donor atom. The clearest example of this is perhaps the acetonitrile complex, where $\nu(C{\equiv}N)$ varies from 2295 cm^{-1} in the free ligand to 2334 cm^{-1} in the coordinated ligand. For urea, $\nu(C{=}O)$ occur at 1605, 1684 cm^{-1} in the free ligand and 1568, 1636 cm^{-1} in the complex. For trimethylphosphate, $\nu(P{=}O)$ shifts from 1263 cm^{-1} (free) to 1212 cm^{-1} (bound). These type of minor shifts are characteristic of coordination to a highly charged metal ion [16].

Except for methanol, all the O-bound ligand complexes are hydrolyzed only slowly in aqueous acid (Table III). Aquation rate constants are within a factor of ten of those reported [6, 7, 17–20] for cobalt(III) analogues. There is from this data alone no clear mechanistic difference between the cobalt(III) and chromium(III) systems. Activation volumes and entropies for the cobalt(III) complexes have been reported [21], and these are being pursued for the chromium(III) complexes at present [22]. Comparisons of these parameters offer a far better opportunity to assess the mechanistic differences purported to exist [2]. The methanol complex is exceptional, since it appears to aquate ~10^3-fold faster than its cobalt(III) analogue. Electronic and infrared spectroscopy is consistent with the formulation of the isolated complex as a methanol complex, yet the kinetic lability is unexpected. The behaviour of this and other alcohol complexes will be pursued, since there are no obvious reasons for the observed behaviour.

The N-donor complexes of imidazole and acetonitrile in acid are exceedingly resistent to hydrolysis. The imidazole complex shows a first-order hydrolysis process with a rate constant equiv-

TABLE III. Rate Constants for Aquation of Pentaamminechromium(III) and Pentaamminecobalt(III) Complexes of Neutral O-Bound Ligands at 25 °C.

Ligand	$k_{aq}(Cr^{III})$, s^{-1}	Ref.	$k_{aq}(Co^{III})$, s^{-1}	Ref.
OH_2	5.2×10^{-5}	17	5.9×10^{-6}	17
$OHCH_3$	5.0×10^{-2}	[a]	6.5×10^{-5}	5
$OS(CH_3)_2$	$1.9_5 \times 10^{-5}$	[a]	1.8×10^{-5}	19
$OP(OCH_3)_3$	6.0×10^{-5}	[a]	2.5×10^{-4}	18
$OC(NH_2)_2$	2.0×10^{-5}	[a]	5.5×10^{-5}	5
$OC(NHCH_3)_2$	1.0×10^{-5}	[a]	5.1×10^{-5}	5
$OCH{\bullet}NH_2$	5.1×10^{-5}	[a]	5.8×10^{-6}	5
$OCH{\cdot}N(CH_3)_2$	$1.4_5 \times 10^{-5}$	[a]	1.6×10^{-6}	20
$OC(CH_3){\cdot}N(CH_3)_2$	1.9×10^{-5}	[a]	8.7×10^{-5}	[a]

[a] This work, standard error <±3%.

alent to ~1.5×10^{-7} s^{-1} at 25 °C. Since the hexaammine complex aquates with a rate constant of 1.7×10^{-7} s^{-1} at 25 °C [12], it is likely that the hydrolysis involves ammonia loss rather than imidazole loss, or at least a competitive hydrolysis could occur. Given the inertness of the complex, this aspect was not pursued.

Clearly, syntheses via the trifluoromethanesulfonato complex offer facile routes to an extended range of chromium(III) complexes of neutral ligands, and aspects of the reactivity of several of these complexes is under study. The techniques applied here to the simple pentaammine can be extended to other unidentate amine complexes [23], and to multidentate amine complexes [7]. Thus, a new, facile and general route to complexes of coordinating solvents and neutral ligands has been established.

References

1 *Spec. Period. Rep.: Inorg. Chem. Transit. Elements,* Vols. 1–6, 1972–1978.
2 *Spec Period. Rep.: Inorg. React. Mech.,* Vols. 1–7, 1971–1980.
3 J. O. Edwards, F. Monacelli and G. Ortaggi, *Inorg. Chim. Acta, 11,* 47 (1974).
4 N. E. Dixon, W. G. Jackson, M. J. Lancaster, G. A. Lawrance and A. M. Sargeson, *Inorg. Chem., 20,* 470 (1981).
5 N. E. Dixon, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem., 22,* 846 (1983).
6 N. E. Dixon, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem., 23,* 2940 (1984).
7 N. J. Curtis, G. A. Lawrance and A. M. Sargeson, *Aust. J. Chem., 36,* 1495 (1983).
8 N. Al-Shatti, T. Ramasami and A. Sykes, *J. Chem. Soc., Dalton Trans.,* 74 (1977).
9 M. Mori, *Inorg. Synth., 5,* 132 (1957).
10 P. Riccierri and E. Zinato, *J. Inorg. Nucl. Chem., 43,* 739 (1981).
11 R. J. Balahura and R. B. Jordan, *Inorg. Chem., 9,* 1567 (1970).
12 J. Bjerrum and C. G. Lamm, *Acta Chem. Scand., 9,* 216 (1955).
13 A. M. Newton and T. W. Swaddle, *Can. J. Chem., 52,* 2751 (1974).
14 H. Burger, K. Burczyk and M. Blaschette, *Monatsch. Chem., 101,* 102 (1970).
15 R. Mecke and F. Langenbucher, 'Infrared Spectra of Selected Chemical Compounds, Vols. I–VIII', Heyden, London, 1965.
16 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1963.
17 T. W. Swaddle and D. R. Stranks, *J. Am. Chem. Soc., 94,* 8357 (1972).
18 W. Schmidt and H. Taube, *Inorg. Chem., 2,* 698 (1963).
19 W. L. Reynolds, M. Birus and S. Asperger, *J. Chem. Soc., Dalton Trans.,* 716 (1974).
20 W. L. Reynolds and M. A. Knoll, *Int. J. Chem. Kinet., 8,* 389 (1976).
21 G. A. Lawrance, *Inorg. Chem., 21,* 3687 (1982).
22 N. J. Curtis, G. A. Lawrance and R. van Eldik, work in progress.
23 N. J. Curtis and G. A. Lawrance, unpublished observations.