Communications

(Trifluoromethanesulfonato-*O*)pentaammine Complexes: Versatile Synthetic Intermediates

Sir:

The use of the triflate (trifluoromethanesulfonato) ligand in synthetic inorganic chemistry has now been well demonstrated for Co(III).[1–4] Either reaction of $[Co(NH_3)_5Cl]Cl_2$ in neat CF_3SO_3H[1] or the solid-state reaction of $[Co(NH_3)_5OH_2](CF_3SO_3)_3$ at elevated temperatures[4] yielded the desired $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ complex. We have now found that the $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_n$ complexes of Cr(III), Rh(III), Ir(III), Ru(III), and Pt(IV) can be obtained by analogous techniques and offer potential as versatile synthetic intermediates.

Apart from the Cr(III) complex, the triflato complexes were obtained by the reactions of the corresponding chloro complexes at 90–110 °C in CF_3SO_3H for several hours followed by the careful addition of diethyl ether at 5 °C to precipitate the product, essentially in quantitative yield. Complete reaction can be assessed by cessation of HCl evolution.[1] The reaction of the Cr(III) chloro complex in neat CF_3SO_3H must be performed at room temperature for a period of ~3 days in order to prevent competitive ammine loss.

The complexes were characterized by microanalysis, by IR and absorption spectroscopy, and by ^1H NMR spectroscopy. Neat CF_3SO_3H was employed as solvent for absorption spectra and NMR spectra, since spectral properties of the triflato complexes are not complicated by substitution reactions in that solvent.

The pentaammine complexes of Rh(III), Ir(III), Cr(III), Ru(III), and Pt(IV) show simple infrared spectra with bands due to amine and triflate.[1] Absorption bands in the IR spectra attributed to the triflate group were split due to the presence of both the coordinated triflato ligand and the triflate counterion bands. In particular, new bands in the region 1300–1420 cm^{-1} appear, which are characteristic of the asymmetric S=O sulfonate ester (RSO_2OR') stretches[5] and have been assigned to the same vibration in the coordinated triflate group. These extra peaks disappear on substitution of the triflato ligand by another ligand in $[M(NH_3)_5L](CF_3SO_3)_n$ complexes. The triflato complexes aquate in dilute acid to yield only one product, detected chromatographically and exhibiting an absorption spectrum consistent with the formation of the aqua complex. No chloride ion could be detected in the isolated complexes. These observations are consistent with initial complete replacement of coordinated and ionic chloride ions by triflate ions while all ammonia ligands are retained.

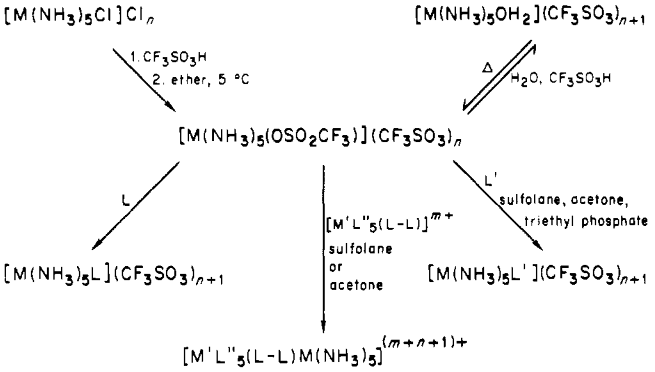
Electronic spectral data of the complexes in this medium are contained in Table I. Examination of the data show that the triflato ligand is a weak field ligand (intermediate between Cl^- and N_3^-). ^1H NMR spectra were obtained for the diamagnetic d^6 complexes and the following chemical shifts (ppm) were observed against sodium 3-(trimethylsilyl)propanesulfonate as internal standard: Co(III), 3.33 (cis), 1.67 (trans); Rh(III), 3.16 (cis), 2.90 (trans); Ir(III), 3.85 (cis and trans); Pt(IV), 4.70 (cis and trans, $J_{^{195}Pt-^1H}$ ~ 100 Hz).

Table I. Aquation Rate Constants at 25 °C and Electronic Spectral Properties of the $[M(NH_3)_5(OSO_2CF_3)]^{n+}$ Complexes

metal ion	k_{aq},[a] s^{-1}	λ, nm (ε, M^{-1} cm^{-1})[b]	ref
Co(III)	$2.6_8 \times 10^{-2}$	345 (40.6), 465 sh (33), 524 (45.8)	1
Rh(III)	$1.8_9 \times 10^{-2}$	267 (84), 333 (103)	*c*
Ir(III)	$1.6_1 \times 10^{-4}$	270 (220), 315 sh (150)	*c*
Cr(III)	$1.2_4 \times 10^{-2}$	364 (31.7), 499 (36.8)	*c*
Ru(III)	$9.3_0 \times 10^{-2}$	284 (790)	*c*
Os(III)	1.6×10^{-3}	235.5 (844), 290 sh (108), 447 (55)	7
Pt(IV)	2.1×10^{-3}	299 (186)	*c*

[a] Average of at least three independent runs; average standard error ≤8%; 0.1 M CF_3SO_3H. [b] Neat CF_3SO_3H. [c] This work.

Scheme I



L = $OHCH_3$, $OS(CH_3)_2$, $NCCH_3$, $OCHN(CH_3)_2$; L′ = $OC(NH_2)_2$, imidazole; L″ = amine; L-L = 4,4′-bipyridine, 1,4-pyrazine

A combination of the weak ligand field exerted by the triflate ligand and its low degree of covalent bonding[6] makes it one of the best leaving groups in inorganic chemistry. This property allows a unique comparison of the substitution kinetics of these normally inert metal ions and also of the recently prepared Os(III) complex.[7] For instance, the rate constants for aquation at 25 °C (0.1 M CF_3SO_3H) are contained in Table I, where a reactivity order of Ru(III) > Co(III) > Rh(III) > Cr(III) > Pt(IV) > Ir(III) is observed. The value for the Pt(IV) complex may contain a degree of base catalysis at this pH value because of the high acidity of amine groups coordinated to Pt(IV). However, two trends in reactivity are apparent. Namely, the rate constant ratios in the Co triad are similar to those normally found,[8] with k_{aq} values in the order Co(III) ≳ Rh(III) ≫ Ir(III), and a 100-fold decrease in rate constant was observed in going from a second-row transition element (Rh(III), Ru(III)) to the corresponding third-row element (Ir(III), Os(III)). Aquation rate constants for the $[M(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$ ions (M = Co(III), Rh(III), Cr(III)) have been determined, and $k(NH_2CH_3)/k(NH_3)$ ratios were found to be 4.2, 1.7, and 0.051 for the Co(III), Rh(III), and Cr(III) complexes, respectively. These manifestations of steric bulk in the amine ligands support the notion that substitution in Co(III) has largely dissociative

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(1) Dixon, N. E.; Jackson, W. G.; Lancaster, M. A.; Lawrance, G. A.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470.
(2) Buckingham, D. A.; Creswell, P. J.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 1647.
(3) Laird, J. L.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 855.
(4) Kupferschmidt, W. C.; Jordan, R. B. *Inorg. Chem.* **1982**, *21*, 2089.
(5) Dolphin, D.; Wick, A. "Tabulation of Infrared Spectral Data"; Wiley: New York, 1977; Chapter 7.1, p 469.
(6) Dixon, N. E.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M., unpublished observations.
(7) Lay, P. A.; Magnuson, R. H.; Sen, J.; Taube, H. *J. Am. Chem. Soc.* **1982**, *104*, 7658.
(8) Edwards, J. O.; Monacelli, F.; Ortaggi, G. *Inorg. Chim. Acta* **1974**, *11*, 47.

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character while Cr(III) exhibits some associative character, with Rh(III) being intermediate. At least they show that the degree of association between the complex and the entering aqua ligand in the transition state follows the order Co(III) < Rh(III) < Cr(III). Detailed comparisons of spontaneous and base-catalyzed substitution kinetics are under way and should provide mechanistic insights for the metal ions in question.

The triflato complexes are extremely versatile synthetic intermediates, and their general reactivity is summarized in Scheme I. When dissolved, the triflato ligand of the complexes was substituted for a molecule of the solvent, to produce the coordinated solvent species in quantitative yields. Other neutral ligands may be substituted by reactions of the triflato complexes in sulfolane, acetone, or triethyl phosphate with the appropriate ligand, since any solvent complexes initially formed are also comparatively labile for these solvents. These procedures have been extended to include the synthesis of binuclear species.[6,7,9] Finally, the synthesis of isotopically labeled complexes such as the $[M(NH_3)_5(^*OH_2)]^{3+}$ ions, in quantitative yields, without isotopic dilution of the residual solvent is a useful attribute.[10]

In summary, the triflato complexes have many desirable properties that make them the most versatile synthetic intermediates presently available for the more substitution-inert metal ions. These properties include (i) air stability, which allows ready handling in air and storage for months in a desiccator without noticeable decomposition, (ii) thermal and shock stability unlike the case of explosive perchlorato complexes[11] of similar lability, (iii) high to moderate solubility and comparatively rapid substitution kinetics in a wide variety of polar solvents, (iv) essentially quantitative syntheses from the readily available $[M(NH_3)_5Cl]Cl_n$ complexes, and (v) ready regeneration from other pentaammine complexes, by thermal reactions, either in the solid state (e.g., $[M(NH_3)_5(OH_2)]$-$(CF_3SO_3)_m$) or in neat CF_3SO_3H.

Registry No. $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-57-9; $[Ir(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-59-1; $[Cr(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-61-5; $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84278-98-8; $[Pt(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_3$, 84254-63-7; $[Co(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$, 84254-64-8; $[Rh(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$, 84254-65-9; $[Cr(NH_2CH_3)_5(OSO_2CF_3)]^{2+}$, 84254-66-0; $[Cr(NH_3)_5Cl]Cl_2$, 13820-89-8; $[Rh(NH_3)_5Cl]Cl_2$, 13820-95-6; $[Ir(NH_3)_5Cl]Cl_2$, 15742-38-8; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $[Pt(NH_3)_5Cl]Cl_3$, 16893-11-1.

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(9) Magnuson, R. H.; Lay, P. A.; Taube, H., submitted for publication in *J. Am. Chem. Soc.*

(10) Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 70.

(11) Harrowfield, J. MacB.; Sargeson, A. M.; Singh, B.; Sullivan, J. C. *Inorg. Chem.* **1975**, *14*, 2864.

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A Convenient Route to Superoxide Ion in Aqueous Solution

Sir:

The aqueous chemistry of the superoxide radical anion is of considerable chemical interest for several reasons, prominent among which is its role in biological processes.[1-4] Although it is stable in aprotic solvents, and readily prepared therein,[5-7] studies of O_2^- in aqueous media are hampered not only by its inherent instability but also by the specialized techniques required to date for its preparation.

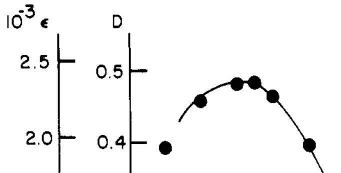

Figure 1. UV absorption spectrum of the long-lived metastable species produced by a 6-s photolysis of Ph_2CO (6.3 μM) in 5.0 M aqueous 2-propanol at pH 12.5 (the absorbance, *D*, was measured in a cell of 2.00-cm optical path). The scales of *D* and of the decadic molar absorptivity, $\epsilon/M^{-1}\ cm^{-1}$, were matched by using $[O_2^-] = 1.02 \times 10^{-4}$ M, calculated from the values of ε given[13b] for λ 230–270 nm; the latter are shown as solid points.

Enzymatic reactions[8] aside, existing methods for the generation of significant concentrations of O_2^- in aqueous or other protic media are limited. Known photochemical methods not only produce O_2^- continuously at a low concentration but also involve highly light-absorbing substances in solution.[9-12] Of the methods described in the literature, only radiolysis (pulse and stopped-flow)[13] and the vacuum-UV photolysis of water[14] produce aqueous O_2^- solutions of appreciable concentration. Reading about the photodissociation of water in aqueous

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(1) (a) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1968**, *243*, 5753. (b) Knowles, P. F.; Gibson, J. F.; Pick, F. M.; Brick, F.; Bray, R. C. *Biochem. J.* **1969**, *111*, 53.

(2) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1969**, *244*, 6049.

(3) Michelson, A. M.; McCord, J. M.; Fridovich, I. "Superoxide and Superoxide Dismutases"; Academic Press: New York, 1977.

(4) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

(5) (a) Sawyer, D. T.; Roberts, J. L. *J. Electroanal. Chem.* **1966**, *12*, 90. (b) Merritt, M. V.; Sawyer, D. T. *J. Org. Chem.* **1970**, *35*, 2157.

(6) (a) Peters, J. W.; Foote, C. S. *J. Am. Chem. Soc.* **1976**, *98*, 873. (b) McElroy, A. D.; Hashman, J. S. *Inorg. Chem.* **1964**, *3*, 1798.

(7) (a) Valentine, J. S.; Curtin, A. B. *J. Am. Chem. Soc.* **1975**, *97*, 224. (b) Matsushita, T.; Shono, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3743.

(8) Bray, R. C. *Biochem. J.* **1961**, *81*, 189.

(9) Organic compounds such as flavins,[10] chemically and photochemically reduced dyes,[11] and certain aromatic compounds[11b,12] undergo one-electron transfer to O_2 (Lee-Ruff, E. *Chem. Soc. Rev.* **1977**, *6*, 195). These reactions have mostly been used for the production of continuous low concentrations of O_2^- in the presence of the desired substrate. These systems are less than ideal for the preparation of O_2^-, however, owing to the high light absorption of the dyes and to possible reactions of O_2^- with the precursors themselves.

(10) (a) Beauchamp, C.; Fridovich, I. *Anal. Biochem.* **1971**, *44*, 276. (b) Massey, V.; Strickland, S.; Mayhew, S. G.; Howell, L. G.; Engel, P. C.; Mathews, R. G.; Schuman, G.; Sullivan, P. A. *Biochem. Biophys. Res. Commun.* **1969**, *36*, 891.

(11) (a) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1972**, *245*, 1374. (b) Balny, C.; Douzon, P. *Biochem. Biophys. Res. Commun.* **1974**, *56*, 386. (c) Jahnke, L. S.; Frenkel, A. W. *Ibid.* **1975**, *66*, 144.

(12) (a) Kodratoff, Y.; Naccache, C.; Imeliki, B. *J. Chem. Phys.* **1968**, *65*, 562. (b) Misra, H. P.; Fridovich, I. *J. Biol. Chem.* **1972**, *247*, 188, 3170.

(13) (a) Bielski, B. H. J.; Gebicki, J. M. *Adv. Radiat. Chem.* **1970**, *2*, 177. (b) Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645. (c) Ilan, Y. A.; Meisel, D.; Czapski, G. *Isr. J. Chem.* **1974**, *12*, 891. (d) Bielski, B. H. J.; Richter, H. W. *J. Am. Chem. Soc.* **1977**, *99*, 3019.

(14) (a) Holroyd, R. A.; Bielski, B. H. J. *J. Am. Chem. Soc.* **1978**, *100*, 5796. (b) Gebicki, J. M.; Bielski, B. H. J. *Ibid.* **1982**, *104*, 796.

0020-1669/83/1322-0847$01.50/0