(27) U. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974).
(28) F. Nordmeyer and H. Taube, *J. Am. Chem. Soc.*, **90**, 1162 (1968).
(29) A very rapid reaction of Cr^{2+} with the primary Cr(III) product, leading to isomerization, must likewise be considered improbable, for it has been noted[26] that reductions, with Cr^{2+}, of $(NH_3)_5Co^{III}$ derivatives are invariably more rapid than the corresponding reactions with $(H_2O)_5Cr^{III}$ derivatives under comparable conditions, although the ratios of specific rates for the two acceptor centers may vary greatly.
(30) The possibility that attack by Cr^{2+} has occurred at a carbanion center at the α position of the chain, generated in response to the acid-strengthening action of the adjacent pyridinium substituent, is inconsistent both with the absence of a $[H^+]$-dependent term in the rate law and with the observed spectra of the Cr(III) products, which are quite unlike those of carbon-bound $(H_2O)_5Cr^{III}$ derivatives (see, for example, M. R. Hyde and J. H. Espenson, *J. Am. Chem. Soc.*, **98**, 4463 (1976)).
(31) See, for example: P. R. Story and B. C. Clark, Jr., in "Carbonium Ions", Vol. 3, G. A. Olah and P. V. R. Schleyer, Eds., Wiley-Interscience, New York, 1972, Chapter 23.
(32) See, for example: J. W. Wilt in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, pp 466–480.
(33) Examples of interactions through space in carbonium ion systems have been compiled by Story and Clark.[31] For a description of such an effect in a free radical system, see W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.*, **98**, 3055 (1976). Further extension to electron-transfer systems has been reported by C. A. Stein and H. Taube, *ibid.*, **100**, 1635 (1978). Such interactions are sometimes described as transannular effects since the groups involved are often incorporated into a ring. Such a description does not properly apply to the interactions in the present study.
(34) M.-Y. Wu, S. J. Paton, Y.-T. Fanchiang, E. Gelerinter, and E. S. Gould, *Inorg. Chem.*, **17**, 326 (1978).
(35) Values of log *k* for reactions of pyridine-derived radicals with Co(III) centers have been found to be linearly related to the formal potentials of these radicals,[36] with a 0.40-V difference in potential corresponding to about a 10^2-fold acceleration. If it be assumed that a similar relationship holds for reactions with Cr(III) centers, the "back-electron-transfer" in X, resulting in its nonproductive dissociation, may be estimated to proceed at a specific rate near 6 s^{-1}.
(36) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1827 (1978).
(37) A reviewer reminds us that if the rate of the overall redox reaction is determined by the rate of formation of an intermediate such as X, internal electron transfer to Co(III) must be much more rapid than electron transfer to Cr(III) (which reverses the initial step). It appears that specific rates for internal electron transfer to metal centers within precursor complexes vary over a wide range. Reported values lie in the range 10^{-3}–10^{-2} s^{-1} for Ru(II)–Co(III) systems,[38] approach 10^{-3} for Fe(II)–Co(III) systems,[39] fall between 10^2 and 10^5 for e^-–Co(III) systems,[40] and may be as great as 5×10^5 for some Cr(II)–Co(III) systems.[41] Since the latter two types most closely resemble systems in the present study, it is reasonable to expect electron transfer to Co(III) to compete very favorably with nonproductive dissociation of the precursor in our more rapid systems.
(38) S. S. Iseid and H. Taube, *J. Am. Chem. Soc.*, **95**, 8198 (1973).
(39) D. Gaswick and A. Haim, *J. Am. Chem.* Soc., **96**, 7845 (1974).
(40) M. G. Simic, M. Z. Hoffman, and N. V. Brezniak, *J. Am. Chem. Soc.*, **99**, 2166 (1977).
(41) H. J. Price and H. Taube, *Inorg. Chem.*, 7, 1 (1968).
(42) In the absence of properly substituted pyridine groups, $(NH_3)_5Co^{III}$ complexes of α-acylamino acids are reduced much more slowly. Thus, k_{Cr} has been found to be 0.30 M^{-1} s^{-1} (25 °C, $\mu = 1.0$) for the acetylglycine complex and 0.57 for the benzoylalanine complex. Corresponding k_{Eu} values are 1.99 and 1.96 M^{-1} s^{-1} (C.A.R., unpublished experiments, 1978).
(43) Unpublished experiments by Dr. S. P.-W. Chum (Kent State University, 1978) in which the parent ligand $Inic^+CH_2COOH$ is used to catalyze the Eu^{2+} reduction of $(NH_3)_5Co(py)^{3+}$ yield the specific rate 166 M^{-1} s^{-1} (25 °C, $\mu = 1.0$) for transfer of an electron to the ligand. This value is, as predicted, remarkably close to that for uncatalyzed reduction of the corresponding $(NH_3)_5Co^{III}$ complex (Table III).

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Electron Transfer. 42. Quinoxalinium Radicals[1]

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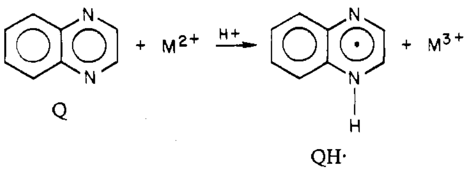
Reduction of quinoxaline with V^{2+}, Eu^{2+}, or Ti^{3+} in 1.2 M $HClO_4$ yields a strongly absorbing yellow species (λ_{max} 357 nm, ϵ 1×10^4), which also exhibits a 15-line ESR spectrum consistent with formulation as the quinoxalinium radical, QH·. Under favorable conditions, this radical persists for over 1 h in aqueous solution. Observed specific rates for the formation of this radical indicate that it is generated by V^{2+} principally via an outer-sphere path but by Eu^{2+} and Ti^{3+} via inner-sphere reductions. Oxidation of the radical by $(NH_3)_5CoBr^{2+}$ proceeds at a rate independent of added quinoxaline, Eu^{3+}, V^{3+}, or Ti(IV), showing that the active species in these reactions is the radical itself, rather than a small quantity of the reducing metal ion in mobile equilibrium with it. The formation of quinoxaline itself, rather than a bromo product, points to an outer-sphere path for this oxidation. It is further found that the quinoxalinium radical does not conform to the linear free-energy relationship which has been found to link the standard potentials of pyridine-related radicals to their outer-sphere reactivities.

The reaction of Cr^{2+} with substituted pyrazines has been shown[1] to yield strongly absorbing chromium(III)-bound radicals, which, in favorable cases, can persist in solution for nearly 1 h. These radical ions reduce one-electron oxidants, and evidence has been presented[2b] that the active intermediate in such reactions is the small quantity of Cr^{2+} in mobile equilibrium with the chromium(III) radical ion. Analogous reductions of pyrazine derivatives with Eu^{2+} and V^{2+} may be envisaged, but since Eu(III) and V(III), in contrast to Cr(III), are labile to substitution in aqueous media, uncomplexed radicals, rather than those stabilized by coordination to metal centers, would be expected to result.

We here report experiments dealing with the quinoxalinium radical, QH·, a species derived from quinoxaline, Q, in acid, which may be handled with much the same ease as the more long-lived chromium(III)–pyrazine radicals.



Q

QH·

M = Eu, V

Experimental Section

Materials. Solutions of chromium(II),[3] europium(II),[4] and vanadium(II)[5] were prepared and analyzed as described. Titanium(III) chloride, available in aqueous solution (Matheson Coleman and Bell) was stirred overnight with zinc amalgam to minimize contamination with Ti(IV) and analyzed for Ti(III) by use of the methods of Martin.[6] Substituted pentaamminecobalt(III) perchlorates not available from previous studies[2b,4,7] were prepared by literature procedures.[7,8] Heterocyclic species (Aldrich products) were used as received except for quinoxaline, which was purified by fractional freezing. Water used as solvent was deoxygenated by boiling deionized water for at least 1 h and was then sealed in a flask and purged with deaerated nitrogen for several hours. All reactions were carried out under nitrogen.

Preliminary Observations. The reduced quinoxaline products in this study were generated by mixing solutions of the reducing agent and the quinoxaline derivative, both in 1 M $HClO_4$. Reductions with Eu^{2+}, like the Cr^{2+}–pyrazine reactions described earlier,[2b] were almost immediate with both reagents at the 0.01 M level, whereas reductions with V^{2+} and Ti^{3+} proceeded at measurable rates. The yellow-green Cr^{2+}–quinoxaline product exhibited a maximum at 647 nm (ϵ 230) and a shoulder at 440 nm, but the yellow quinoxaline products with Eu^{2+}, V^{2+}, and Ti^{3+} displayed a single maximum at 357 nm (ϵ 1.0 $\times 10^4$ in each case). Spectrophotometric titration of quinoxaline with each of the reductants indicated that maximal absorbance occurred at a 1:1 ratio of reactants and that further addition of reductant

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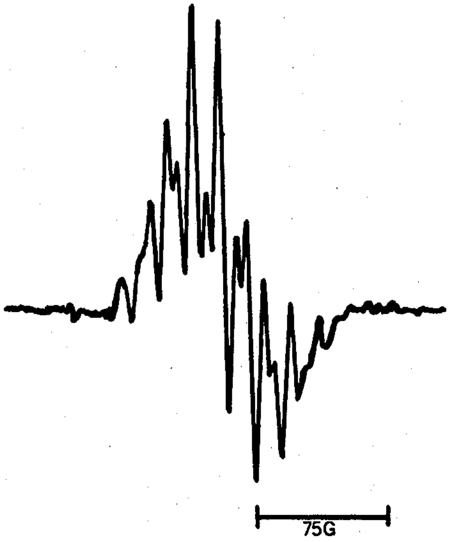

Figure 1. ESR spectrum of the quinoxalinium radical (Varian V-4500 X-band spectrometer) in 90% aqueous ethanol. Generating solution was 0.005 M in quinoxaline, 0.0025 M in $V(ClO_4)_2$, and 1.2 M in $HClO_4$. Spectrum was taken 15 min after mixing. Virtually identical spectra were obtained when $Eu(ClO_4)_2$ or $TiCl_3$ was substituted for $V(ClO_4)_2$. Center of spectrum is at $g = 1.99$.

resulted in rapid fading. The Cr^{2+} product was obviously different from that obtained from the other reductants and was much less stable. It was not studied further.

For ESR measurements, with a Varian V-4500 X-band spectrometer, solutions were made in 90% aqueous ethanol and were 0.005 M in quinoxaline, 0.0025 M in Eu^{2+}, V^{2+}, or Ti^{3+}, and 1 M in $HClO_4$. Nearly identical 15-line spectra centered near $g = 1.99$ (Figure 1) were obtained with these three reductants. The spectra persisted for nearly 60 min at 25 °C in systems from which O_2 was rigorously excluded.

The yellow quinoxaline species reacted with the various halopentaamminecobalt(III) complexes and with the azido, *N*,*N*-diethylnicotinamide, 4-benzoylpyridine, and 3-acetylpyridine derivatives of $(NH_3)_5Co^{III}$, yielding equivalent quantities of Co^{2+}. Straightforward kinetic behavior was observed only in the reactions of $(NH_3)_5CoBr^{2+}$; the source of difficulty with the other oxidants, which persisted despite several modifications in procedure, is not clear. Nevertheless, it was evident that the remaining halo complexes and the azido complex reacted at specific rates near that for the bromo derivative and that the 4-benzoylpyridine complex reacted much more rapidly. Reactions with the formato, maleato, and pyruvato complexes of $(NH_3)_5Co^{III}$ were much slower and gave less than stoichiometric amounts of Co^{2+}. In instances where the yellow species was allowed to react with an equivalent quantity of Co(III) in the absence of excess quinoxaline, it could be regenerated, with only slight loss, by readdition of reductant.

Rate Measurements. Rates of formation of the yellow quinoxaline species and its reaction with Co(III) oxidants were estimated from measurements of absorbance changes on a Cary 14 recording spectrophotometer.[2b] Both types of measurements were carried out in the presence of a known excess of quinoxaline. Measurements of the formation of the yellow radical were made at 357 nm, and those of reactions with Co(III) complexes at the low-energy peak for the oxidant (550 nm for the bromo complex). Formation of the radical was first order both in quinoxaline and in reductant. Reactions with $(NH_3)_5CoBr^{2+}$ were first order in radical (hence first order in added reductant) and first order in Co(III) and were inhibited neither by excess quinoxaline nor by added Eu^{3+}, V^{3+}, or Ti(IV). The supporting electrolyte was generally 1.0 M $HClO_4$. Reactions were generally followed for at least 4 half-lives, and pseudo-first-order rate constants were calculated from logarithmic plots of absorbance differences against reaction time. Specific rates obtained from replicate runs with the bromo oxidant checked to within 8%. Temperatures were kept at 25.0 ± 0.2 °C during the entire series of experiments.

Comparison of Stabilities. Approximate comparison of the stabilities of various reduced quinoxaline preparations was carried out, in a manner similar to that described,[2b] by allowing solutions to stand for known time periods under nitrogen, adding $(NH_3)_5CoCl^{2+}$, and then estimating the quantity of Co^{2+} released. Samples (0.033 mmol) of the heterocycles were dissolved in 1.4 mL of 1.2 M $HClO_4$, 0.030 mmol of $Eu(ClO_4)_2$ was added, and, after a measured waiting period, a saturated solution of $(NH_3)_5CoCl(ClO_4)_2$ was added until the maroon color of the Co(III) persisted. The sample was then diluted to 25.0 mL with concentrated HCl, the absorbance at 692 nm was read, and the number of moles of Co(II) was calculated.[3] Results are summarized in Table I. The colored species were found to be much less stable in 0.05 M than in 1.2 M $HClO_4$, but the manner in which they decompose at the lower acidity was not determined. These decompositions were not appreciably more rapid in direct sunlight than in the dark.

Table I. Stabilities of Heterocyclic Radicals

heterocyclic base	reducing power recovered, %^{a}
pyrazinecarboxamide	11^b
methylpyrazine	31^c
2,3-pyrazinedicarboxylic acid	33^d
pyrazine	40^e
2,5-dimethylpyrazine	73^c
2,6-dimethylpyrazine	77^c
pyrazinetetracarboxylic acid	80^f
	20^g
cinnoline-4-carboxylic acid	96^g
2,3-dimethylquinoxaline	84
	82^g
quinoxaline	97
	95^g
	95^h

[a] 0.033 mmol of base and 0.30 mmol of Eu^{2+} in 1.5 mL of 1.2 M $HClO_4$; waiting period 30 s unless otherwise indicated (see text). [b] Yellow-green before addition of Co(III). [c] Pink before addition of Co(III). [d] Yellow precipitate formed. [e] Lavender before addition of Co(III). [f] Orange before addition of Co(III). [g] Waiting period 10 min. [h] Waiting period 20 min.

Results and Discussion

Although quinoxaline ($pK_a = 0.56$)[9] is only partially protonated in 1.2 M $HClO_4$, addition of an electron to the ring system should markedly increase the basicity of the nitrogens.[10] The reduced (radical) form is doubtless nearly fully protonated in our solutions and is represented as structure QH·. The ESR spectrum detected with each of the reduced preparations (Figure 1) is consistent with this formulation, with the observed 15-fold (5 × 3) hyperfine splitting attributable to the combined action of the two nitrogens (each with $I = 1$) and the two α-hydrogens (each with $I = {}^1/_2$). Further splitting by the acidic hydrogen, which exchanges rapidly with solvent, is not to be expected.[11] The spectra resulting from reductions by Eu^{2+} and V^{2+} are identical with those resulting from reduction by Ti^{3+}, showing that magnetic interaction between the radical center and the unpaired d electrons of V^{3+}, or the unpaired f electrons of Eu^{3+}, is negligible.

Representative kinetic data, for the formation of the quinoxalinium radical from the V^{2+} reduction and for the oxidation of the radical with $(NH_3)_5CoBr^{2+}$, are listed in Table II. Both processes appear to conform to straightforward second-order rate expressions, and this simplicity extends to the corresponding Eu^{2+} and Ti^{3+} systems. Calculated specific rates for radical formation, and for its oxidation by $(NH_3)_5CoBr^{2+}$, are assembled in Table III. Note that the formation of the radical from the reduction by Eu^{2+} is so rapid that only a lower limit (obtained by assuming the reaction to be bimolecular) is entered.

The specific rate for the reduction by vanadium(II), $1.7 \times 10^3\ M^{-1}\ s^{-1}$, lies far above 20–40 $M^{-1}\ s^{-1}$, the substitution-controlled upper limit for inner-sphere reductions by this reagent under our conditions.[12] This process may then be taken to proceed nearly completely by an outer-sphere path. If reduction by Eu^{2+} was also principally outer-sphere, one would expect, on the basis of previous experience with diverse

Table II. Kinetic Data for Formation of the Quinoxalinium Radical and Its Oxidation by $(NH_3)_5CoBr^{2+}$ [a]

A. Formation: $Q + V^{2+} + H^+ \rightarrow QH\cdot + V^{3+}$

$10^6[V^{2+}]$	$10^5[Q]$	$10^5[V^{3+}]$	$10^{-3}k$ [b]
2.50	1.25	0	1.60
1.25	1.25	0	1.70
2.50	2.50	0	1.42
2.50	5.00	0	1.64
2.50	10.0	0	1.81
2.50	2.50	1.0	1.76
2.50	2.50	2.5	1.75

B. Oxidation: $QH\cdot + (NH_3)_5CoBr^{2+} + 4H^+ \rightarrow$ $Q + 5NH_4^+ + Co^{2+} + Br^-$

$10^3 \times [Co^{III}]$	$10^4[V^{2+}]_0$ [c]	$10^3[Q]_0$ [d]	$10^4[V^{3+}]$	k [e]
1.67	3.3	5.3	0	8.3
3.30	6.7	5.3	0	7.9
6.70	6.7	5.3	0	8.4
13.3	6.7	5.3	0	8.4
6.70	6.7	1.33	0	8.8
6.70	6.7	2.70	0	9.0
6.70	6.7	10.7	0	8.6
6.70	6.7	21.3	0	8.7
6.70	6.7	5.3	6.7	7.8
6.70	6.7	5.3	13.3	7.9
6.70	6.7	5.3	67	7.7
6.70	6.7	5.3	133	7.8
6.70	6.7	5.3	0	8.2 [f]

[a] Rate measurements at 25 °C in 1.0 M $HClO_4$. Concentrations in molar units. [b] Specific rate, in $M^{-1}\ s^{-1}$, defined as $(d[QH\cdot]/dt)\cdot[V^{2+}]^{-1}[Q]^{-1}$. [c] Concentration of V^{2+} used to generate $QH\cdot$. [d] Concentration of quinoxaline used to generate $QH\cdot$. [e] Specific rate, in $M^{-1}\ s^{-1}$, defined as $(-d[QH\cdot]/dt)[Co^{III}]^{-1}[QH\cdot]^{-1}$. [f] Solution 0.08 M in Cl^-.

Table III. Specific Rates for Formation of the Quinoxalinium Radical and Its Oxidation by $(NH_3)_5CoBr^{2+}$ [a]

reductant	k_{formn}	k_{oxidn}
Eu^{2+}	$>2.5 \times 10^4$	9.0 ± 0.3
V^{2+}	1.7×10^3	8.3 ± 0.4
Ti(III)	0.44	5.6 ± 0.6

[a] Measurements at 25 °C; supporting electrolyte was 1 M $HClO_4$. Reactions given and specific rates ($M^{-1}\ s^{-1}$) defined in Table I.

outer-sphere series,[13,14] its specific rate to be about one-third that for V^{2+}. Since however, the ratio k_{Eu}/k_V is found to be >14, we may infer the predominance of an inner-sphere component in this case.

Arguments pertaining to the reduction by Ti^{3+} are less direct. Extension of the treatment of Thompson and Sykes[15] leads to relationship (1) which applies, in an approximate

$$\log k_{Ti} = 0.55 \log k_V - 3.4 \qquad (1)$$

fashion, to outer-sphere reductions by Ti^{3+} and V^{2+} in 1 M H^+.[16-18] This, in conjunction with the observed value of k_V, allows us to estimate an outer-sphere specific rate of 0.025 $M^{-1}\ s^{-1}$ for reduction by Ti^{3+}, a value about $^1/_{20}$th that observed. Hence, a substantial inner-sphere component is likely here also.

Turning now to the oxidation of $QH\cdot$ by $(NH_3)_5CoBr^{2+}$, we note that the reaction is first order in both of these species and is not affected by addition of excess quinoxaline or by added V^{3+}, Eu^{3+}, or Ti(IV). This is strong evidence that the active species in these reactions is the radical itself, formed in a very nearly stoichiometric amount in the preliminary reduction, rather than a small quantity of the reducing metal ion in mobile equilibrium with it, as is the case in Cr(II)–pyrazine system.[2b] As expected, the rate at which $QH\cdot$ is oxidized is essentially independent of whether the radical is generated by the action of Eu^{2+} or V^{2+}. However, the radical in the Ti(III)–Ti(IV) system is found to react about 35% more slowly than that formed from the dipositive oxidant. This apparent inhibition is not due to the presence of chloride in our titanium preparations, for addition of a comparative quantity of Cl^- to the vanadium system is seen not to affect the rate of oxidation (cf. the final entry in Table IIB). Some interaction between the radical and a Ti(IV) species may be occurring, but further evidence on this point is obviously necessary.

The oxidation of $QH\cdot$ by $(NH_3)_5CoBr^{2+}$ appears to give quinoxaline itself, rather than a product in which bromine is bound to the aromatic ring. This indicates that this radical, like a number of pyridine-related radicals that have been examined,[19] reacts with Co(III) centers without ligand transfer, i.e., by an outer-sphere path.[20]

Fanchiang[21] has pointed out that log k values for oxidation of a number of pyridine-derived radicals by a common Co(III) oxidant are linearly related to the formal reduction potentials ($E°$ values) of the parent aromatics. Oxidations by $(NH_3)_5Co(py)^{3+}$, for example, conform to eq 2, a relationship

$$\log k = 3.81 - 5.17E° \qquad (2)$$

formally similar to the Brønsted catalysis law, which however pertains to reactions featuring proton-transfer steps. To determine whether (2) extends to the quinoxalinium radicals, we note that the reduction potential of quinoxaline in 1 M $HClO_4$ has been estimated to be 0.18 V more positive in this medium than that of pyrazine[22] which, from the data of Klatt and Rouseff,[23] may be assigned a value of –0.02 V (vs. NHE). Substitution of $E° = 0.16$ V into (2) leads to an estimated k of $10^3\ M^{-1}\ s^{-1}$ for reaction of $QH\cdot$ with $(NH_3)_5Co(py)^{3+}$. The latter specific rate, however, cannot be considered reasonable since it is 10^2 times as great as the value here observed for reaction of the radical with $(NH_3)_5CoBr^{2+}$, despite evidence from other studies[24] that outer-sphere reductions of the pyridine complex proceed only about 10^{-3} times as rapidly as those of the bromo complex.[25] It may then be concluded that Fanchiang's relationship, as is the case with the Brønsted catalysis law to which it has been likened, is applicable only to series of donors which are structurally similar (e.g., to radicals in which the unpaired electron is accommodated by a pyridine ring).

Registry No. Q, 91-19-0; $QH\cdot$, 69277-70-9; Eu^{2+}, 16910-54-6; V^{2+}, 15121-26-3; Ti^{3+}, 22541-75-9; $(NH_3)_5CoBr^{2+}$, 14970-15-1; pyrazinecarboxamide, 98-96-4; methylpyrazine, 109-08-0; 2,3-pyrazinedicarboxylic acid, 89-01-0; pyrazine, 290-37-9; 2,5-dimethylpyrazine, 123-32-0; 2,6-dimethylpyrazine, 108-50-9; pyrazinetetracarboxylic acid, 43193-60-8; cinnoline-4-carboxylic acid, 21905-86-2; 2,3-dimethylquinoxaline, 2379-55-7; $(NH_3)_5CoCl^{2+}$, 14970-14-0.

References and Notes

(1) Sponsorship of this work by the National Science Foundation (Grant CHE77-14950) is gratefully acknowledged.

(2) (a) H. Spiecker and K. Wieghardt, *Inorg. Chem.*, **16**, 1290 (1977); (b) M.-Y. Wu, S. J. Paton, Y.-T. Fanchiang, E. Gelerinter, and E. S. Gould, *ibid.*, **17**, 326 (1978).

(3) E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

(4) (a) E. R. Dockal and E. S. Gould, *J. Am. Chem. Soc.*, **94**, 6673 (1972); (b) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974).

(5) (a) P. R. Guenther and R. G. Linck, *J. Am. Chem. Soc.*, **91**, 3769 (1969); (b) R. G. Linck, *Inorg. Chem.*, **9**, 2529 (1970).

(6) A. H. Martin and E. S. Gould, *Inorg. Chem.*, **14**, 873 (1975).

(7) E. S. Gould, N. A. Johnson, and R. B. Morland, *Inorg. Chem.*, **15**, 1929 (1976).

(8) (a) M. Linhard and H. Flygare, *Z. Anorg. Allg. Chem.*, **262**, 328 (1950); (b) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 495 (1963).

(9) A. Albert in "Physical Methods in Heterocyclic Chemistry", Vol. 1, A. R. Katritzky, Ed., Academic Press, New York, 1963, p 84. The value quoted was measured at 20 °C.

(10) U. Bruhlmann and E. Hayon, *J. Am. Chem. Soc.*, **96**, 6169 (1974), have shown, for example, that the pK_a of the radical derived from one-electron reduction of nicotinamide is 13.4, i.e., 10 units greater than that of nicotinamide itself. A similar increase in pK_a was noted on reduction of 3-acetylpyridine.

(11) For a detailed ESR study of the *basic* form of the quinoxaline radical, Q·, a species which is generally prepared in nonaqueous media, see A. Carrington and J. d. Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

(12) (a) K. W. Hicks, D. L. Toppen, and R. G. Linck, *Inorg. Chem.*, **11**, 310 (1972); (b) J. C. Chen and E. S. Gould, *J. Am. Chem. Soc.*, **95**, 5539 (1973); (c) N. Sutin, *Acc. Chem. Res.*, **1**, 225 (1965).
(13) (a) F.-R. F. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2647 (1974). (b) Y.-T. Fanchiang and E. S. Gould, *ibid.*, **16**, 2516 (1977). (c) Note that the Marcus model[14] stipulates that relative rates of outer-sphere reduction of a given oxidant by two reductants should be independent of the identity of the oxidant.
(14) R. A. Marcus, *Annu. Rev. Phys. Chem.*, **15**, 155 (1964).
(15) (a) G. A. K. Thompson and A. G. Sykes, *Inorg. Chem.*, **15**, 638 (1976). (b) See also M. Hery and K. Wieghardt, *ibid.*, **17**, 1130 (1978).
(16) Equation 1 results from combination of Thompson and Sykes' linear free-energy relationship, which pertains to reductions by the species $TiOH^{2+}$, with the $pK_a = 2.8$ reported for Ti^{3+}(aq) by Krentzien and Brito.[17] We here use the more limited form, applying specifically to 1 M H^+, since decomposition of the quinoxalinium radical at higher pHs appeared to rule out establishment of an inverse-acid dependence in our Ti(III) systems.
(17) H. Krentzien and F. Brito, *Ion (Madrid)*, 14 (1970); *Chem. Abstr.*, **73**, 7865 (1970).
(18) Note that Ti^{III} does not conform to the Marcus model,[14] which predicts a slope of nearly unity (rather than 0.55) when values of log k_{Ti} are plotted against values of log k_V.
(19) (a) H. Cohen and D. Meyerstein, *Isr. J. Chem.*, **12**, 1049 (1974); (b) Y.-T. Fanchiang, R. R. Carlson, P. K. Thamburaj, and E. S. Gould, *J. Am. Chem. Soc.*, **99**, 1073 (1977).
(20) For evidence that pyridine-related radicals may, in favorable cases, undergo inner-sphere oxidations, see, for example, M. Mohammad and E. K. Kosower, *J. Am. Chem. Soc.*, **93**, 2709 (1971).
(21) Y.-T. Fanchiang and E. S. Gould, *Inorg. Chem.*, **17**, 1827 (1978).
(22) Y.-T. Fanchiang, J. C. Thomas, V. D. Neff, J. C.-K. Heh, and E. S. Gould, *Inorg. Chem.*, **16**, 1942 (1977).
(23) L. N. Klatt and R. L. Rouseff, *J. Am. Chem. Soc.*, **94**, 7295 (1972).
(24) J. F. Endicott and H. Taube, *J. Am. Chem. Soc.*, **86**, 1686 (1964), report, for example, that $Ru(NH_3)_6^{2+}$ reduces $(NH_3)_5CoBr^{2+}$ at a specific rate of 1600 M^{-1} s^{-1} (25 °C, $\mu = 0.2$), whereas experiments by Fan[13a] indicate a rate constant near 0.3 M^{-1} s^{-1} for reduction of $(NH_3)_5Co(py)^{3+}$ under comparable conditions. Again, the ratio of specific rates for the two oxidants should be nearly independent of the outer-sphere reductant taken.[14]
(25) The slow decay of the quinoxalinium radical in solution complicates kinetic study of the reactions of this radical with the more sluggish oxidants. In attempted measurements, with [QH·] at the 0.004 M level and $[Co(NH_3)_5(py)^{3+}]$ at the 0.04 M level, it was found that less than 5% of the radical was oxidized in 30 min, indicating a bimolecular redox specific rate less than 0.03 M^{-1} s^{-1} (25 °C, 1.0 M $HClO_4$).

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Reactions of Coordinated Molecules. 18. Complexes of the Triacylmetalate Dianions

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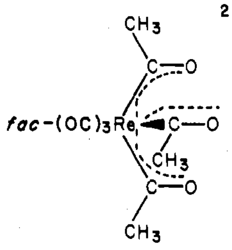
Triacylmetalate dianions of the type $[fac\text{-}(OC)_3Re(CH_3CO)_2(RCO)]^{2-}$, where R is methyl, isopropyl, benzyl, or the bridging ligands $(CH_2)_n$ where n is 5 or 6, are prepared from the corresponding neutral acylpentacarbonylrhenium complexes and 2 equiv of methyllithium. The formation of these anions is followed by IR, and the triacetyl dianion is isolated as the PPN salt. These dianions form bis-chelate complexes with Al(III), Ga(III), Hf(IV), and Zr(IV) metal ions. The aluminum and gallium complexes are anionic while the hafnium and zirconium complexes are neutral. The ligands act as tridentate chelates possessing idealized C_{3v} symmetry. This coordination geometry is confirmed by the observation of geometrical isomers for those complexes having unsymmetrically substituted ligands.

In a previous communication we reported the stoichiometric preparation of the triacetyltricarbonylrhenate dianion $fac\text{-}(OC)_3Re(CH_3CO)_3^{2-}$, **1**, and its coordination to Al(III) and Hf(IV) metal ions.[1] This dianion is a formal, metalla analogue of the triacetylmethanide anion, and it coordinates to metal ions presumably as a symmetrical tridentate chelating ligand as shown in **2**. To our knowledge dianions like **1** are the only known trioxygen ligands which coordinate as vicinal, bifurcated chelates.[2,3] These dianionic ligands also possess a formally π-delocalized electronic system.



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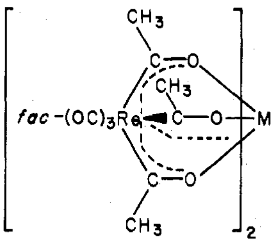

2

We wish to report a general preparative procedure for the synthesis of these metalla ligands and their coordination complexes and to confirm the structure of the metal complexes **2** by demonstrating the existence of the expected geometrical isomerism when one of the alkyl substituents of each ligand is not a methyl group.[4]

The metal complexes **2** represent discrete molecules containing three metal atoms which are connected via unsaturated carbon–oxygen linkages. The central coordinating metal atom may be either a transition-metal or a main-group metal ion. These complexes are related to the metalla-β-diketonate complexes,[4] and they represent another type of polymetallic molecule which lacks direct metal–metal bonding. Such species may be relevant in catalytic processes particularly when multifunctional group activation and protection is required simultaneously.

Experimental Section

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25 °C unless otherwise stated. Diethyl ether, tetrahydrofuran, benzene, toluene, hexane, and pentane were dried over Na/K alloy, and methylene chloride was dried over phosphorus pentoxide under a nitrogen atmosphere. Other solvents were dried over 4A molecular sieves and were purged with nitrogen before use. Decacarbonyldirhenium was purchased from Pressure Chemical Co. (Pittsburgh, PA). Anhydrous gallium trichloride, hafnium tetrachloride, and zirconium tetrachloride were purchased from Ventron Corp. and were handled under an argon atmosphere in a glovebag.

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as methylene chloride solutions in 0.10-mm sodium chloride cavity cells with the solvent as a reference and a polystyrene film as a calibration standard. Band frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a JEOL MH-100 NMR spectrometer with Me_4Si as an internal reference.

Microanalyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN).

$CH_3C(O)Re(CO)_5$,[5] **3**, $(CH_3)_2CHC(O)Re(CO)_5$,[4] **4**, and $C_6H_5CH_2C(O)Re(CO)_5$,[6] **5**, were prepared by slight modifications of known procedures with the pentacarbonylrhenate anion and the appropriate acyl chloride.

General Preparation of $[(OC)_5ReC(O)CH_2]_2(CH_2)_n$ Where n Is 4 or 5. To a stirred solution of $NaRe(CO)_5$ in 50 mL of THF at −78 °C was added dropwise 0.5 molar equiv of the appropriate diacid dichloride. After being stirred at −78 °C for 30 min, the reaction

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