mined the structures of a number of complexes with coordinated nitric oxide.[7] On the basis of their X-ray data and infrared stretching frequencies they[7c] have proposed the following criteria: NO^+ complexes have $\nu(NO)$ in the range 1600–1845 cm^{-1} and for NO^- complexes $\nu(NO)$ is in the range 1525–1720 cm^{-1}. Therefore, it is inadequate to use $\nu(NO)$ solely to determine the mode of coordination in the region 1600–1720 cm^{-1}. We may conclude, however, that NO is coordinated as NO^+ in our nitrosyl complexes.

Reactions of tetracyanoethylene and fumaronitrile with $IrX(CO)(P(C_6H_5)_3)_2$ (X = Cl, Br, I) have been studied extensively.[3] A number of new compounds have been isolated and characterized in these and similar reactions.

TCNE will add to $[IrCl(NO)(P(C_6H_5)_3)_2]^+$ to give $[IrCl(NO)(P(C_6H_5)_3)_2TCNE]ClO_4$. There is a change in the bonding of NO to iridium upon coordination as evidenced by the change in $\nu(NO)$ from 1902 to 1595 cm^{-1}. It seems plausible that this structure would be similar to the bent coordinated NO as determined crystallographically in $[IrCl(CO)(NO)(P(C_6H_5)_3)_2]BF_4$[5] and that NO is coordinated as NO^- here. However, such proposals must be vindicated by crystallographic study.

The addition of the weaker Lewis acid fumaronitrile to $[IrCl(NO)(P(C_6H_5)_3)_2]^+$ produced no reaction, in contrast to $[IrCl(CO)(P(C_6H_5)_3)_2]$ which forms a stable compound.[3] This decrease in chemical reactivity is consistent with previous reports on this complex.[2c] The decrease in apparent chemical reactivity is probably due to the positive charge on the complex and the resultant decrease in electron density on the metal. For example, this complex shows no tendency to combine with O_2,[2c] whereas the uncharged complex $RuCl(NO)(P(C_6H_5)_3)_2$ forms an irreversible adduct with O_2.[8]

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Free Radical Mechanism in the Acid-Catalyzed Redox Decomposition of Tris(oxalato)cobaltate(III) Ion in Aqueous Solution[1]

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Although there has been some dispute concerning the detailed path by which the acid-catalyzed redox decomposition of $Co(C_2O_4)_3^{3-}$ is initiated,[2] there has been general agreement up to now that the overall mechanism involves production of a free radical ($C_2O_4^-$ or CO_2^-) which reattacks the substrate to form additional Co^{2+}.[3–9] In simplest terms this process may be represented

$$Co(C_2O_4)_3^{3-} \xrightarrow{k_1} Co^{2+} + C_2O_4^- + 2C_2O_4^{2-} \qquad (1)$$

$$C_2O_4^- + Co(C_2O_4)_3^{3-} \xrightarrow{k_2} Co^{2+} + 2CO_2 + 3C_2O_4^{2-} \qquad (2)$$

where $Co(C_2O_4)_3^{3-}$ may be taken here to include protonated and ring-opened forms, $C_2O_4^{2-}$ includes $HC_2O_4^-$ and $H_2C_2O_4$, and $C_2O_4^-$ includes its protonated form (or CO_2^- and CO_2H). The basis for this free radical mechanism appears to have arisen largely by analogy to the photochemical decomposition[3,4] and to other oxalate reactions[10] in which free radicals have been implicated. Some additional support has been offered by the observation that the thermal decomposition leads to other processes which are accepted as involving free radicals, such as vinyl polymerization.[3]

Recently Hin-Fat and Higginson[11] have advanced the hypothesis that the thermal decomposition does not involve free radicals at all. The key observation, cited by these authors for both $Co(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_2(H_2O)_2^-$, is a deviation from first-order behavior as seen by curvature in plots of log $(A_t - A_\infty)$ *vs.* time (where A = absorbance). The fact that wholly linear plots could be obtained by addition of a term inverse in complex concentration, together with the effect of changes in reaction conditions on the magnitude of this term, led these authors[11] to favor a mechanism involving a concerted three-center redox reaction between the substrate and a ring-opened species.

At appropriate relative concentrations of the reactive species, with O_2 as an added scavenger, reactions 3 and 4 can predominate over (2), where $2k_4 = 1 \times 10^9\ M^{-1}$

$$C_2O_4^- + O_2 \xrightarrow{k_3} 2CO_2 + O_2^- \qquad (3)$$

$$2C_2O_4^- \xrightarrow{k_4} 2CO_2 + C_2O_4^{2-} \qquad (4)$$

sec^{-1} [12] and (3) is assumed to be very efficient by analogy to the CO_2^-–O_2 reaction.[13] In highly acidic solution, the O_2^- radical will exist in its $H_2O_2^+$ form[14] which does not appear to be effective in reducing simple Co(III) complexes.[15] Thus, the formation of Co^{2+} in the presence of O_2 from secondary radical reactions is of negligible contribution.[16] Here, in the slow thermal

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[2] A detailed discussion, which makes it clear that the initiation process occurs in steps, will be fully presented in a separate communication.

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[16] I. M. Kolthoff, E. J. Meehan, and M. Kimura [*J. Phys. Chem.*, **75**, 3343 (1971)] report that decomposition of acidic solutions of $Co(C_2O_4)_3^{3-}$ in the presence of oxygen leads to the production of H_2O_2, which is presumed to arise from the disproportionation of HO_2.

reaction where the steady-state concentration of the $C_2O_4^-$ radical would be very low, (4) is of no concern. However, it is easy to see that *if the radical mechanism is valid,* then the rate of $Co(C_2O_4)_3^{3-}$ decomposition in deoxygenated solutions would be twice as fast as in the presence of O_2 as long as $k_2[Co(C_2O_4)_3^{3-}] \ll k_3[O_2]$. Where the reverse conditions hold, the presence of O_2 should have no effect on the rate. The solubility of O_2 in an O_2-saturated solution at 1 atm and 25° is approximately 1.3×10^{-3} *M*.

A weighed quantity of $K_3Co(C_2O_4)_3 \cdot 3H_2O$ was dissolved in a cold solution containing a stoichiometric amount of $NaClO_4$ and the resulting $KClO_4$ precipitate was removed. The filtrate was added to thermostated (25.0°) aqueous $HClO_4$ and the solution diluted so that it was 1.08 *M* in acid. One-half of the solution was continuously purged with Cr^{2+}-scrubbed N_2 and the other half was continuously bubbled with H_2O-saturated O_2. The solutions were kept in the dark and thermostated. Aliquots were removed periodically and the loss of complex was followed spectrophotometrically at 243, 420, or 603 nm, the choice of wavelength dictated by the concentration of the complex. There was negligible evaporation of the solutions. The first-order rate constants were obtained from a plot of $\ln [(A_0 - A_\infty)/(A_t - A_\infty)]$ *vs.* time.

Table I shows the observed first-order rate constants in the presence of N_2 and O_2 as a function of the initial concentration of the complex. All plots were linear for at least 1.5 half-lives except in the case of $[Co(C_2O_4)_3^{3-}] < 3 \times 10^{-6}$ *M* in N_2 where curvature was observed after 1 half-life. It is clear that $k_{N_2}/k_{O_2} \rightarrow 1$ as $[O_2]/[Co(C_2O_4)_3^{3-}]_0 \rightarrow 0$ and $k_{N_2}/k_{O_2} \rightarrow 2$ as $[Co(C_2O_4)_3^{3-}]_0/[O_2] \rightarrow 0$. Furthermore, $k_2/k_3 \sim 10$ as obtained from the integrated rate expression for steps 1–3.[17] Thus, our results are in full accord with the free radical mechanism.

TABLE I

RATE CONSTANTS IN THE PRESENCE OF N_2 AND O_2[a]

$[Co(C_2O_4)_3^{3-}]_0$, *M*	Obsd first-order rate constants, 10^5 sec^{-1} [b] k_{N_2}	k_{O_2}	k_{N_2}/k_{O_2}
1.58×10^{-2}	5.23	5.23	1.00
1.02×10^{-3}	5.47	4.35	1.26
2.71×10^{-4}	5.65	3.68	1.53
$(1.17, 1.09) \times 10^{-5}$	5.45[c]	3.21[c]	1.69
$(3.99\text{–}2.41) \times 10^{-6}$	[5.45][d]	2.93[e]	1.86

[a] Temperature 25.0°; 1.08 *M* $HClO_4$. [b] Single determinations unless otherwise noted. [c] Average of two determinations. [d] Average of the five determinations at 10^{-2}–10^{-5} *M*. The kinetic plots at 10^{-6} *M* showed curvature preventing a reliable determination of k_{N_2} in this case. This effect is presumably due to the presence of low concentrations of adventitious impurities. [e] Average of four direct determinations. The kinetic plots showed no curvature within 1.5 half-lives.

The curvature observed by Hin-Fat and Higginson,[11] which led them to reject the free radical mechanism, appears to have a very simple explanation. These authors checked the possible influence of atmospheric O_2 and found none. Failure to see an effect is understandable in light of our results, because in their complex concentration range, the differences in the *initial* rates of reaction in air and in N_2 would be very small (<5%). There is no indication from their paper that solutions were deoxygenated on a regular basis, nor would there have seemed any need to do this. Consequently, under their conditions, (1) and (2) predominate during the initial stages of reaction, but as the extent of reaction increases and $[Co(C_2O_4)_3^{3-}]$ decreases, (3) begins to contribute. Thus, the rate would fall off at high extents of reaction.[18] A first-order plot of their data shows no change in the initial slope upon variation of $[Co(C_2O_4)_3^{3-}]_0$. However, the point where curvature begins advances to shorter extents of reaction as $[Co(C_2O_4)_3^{3-}]_0$ is decreased. This behavior is consistent with the interference of dissolved O_2 *via* reaction 3. *Our results thus appear to remove the experimental basis which led Hin-Fat and Higginson*[11] *to reject the free radical mechanism.*

It must be pointed out that the concerted mechanism proposed by Hin-Fat and Higginson[11] leads to the same form of the rate law as (1)–(3) if it is assumed that the ring-opened species reacts with O_2 and is maintained at a steady-state concentration. For this mechanism to be in accord with our observations would require further that the ring-opened species react with the substrate and O_2 at comparable rates. Maintenance of the ring-opened species at steady-state concentrations is inconsistent with other results we have obtained[2,9] and the idea that such a species would react as rapidly with O_2 as required by our observed rates is simply not in accord with the properties of related Co(III) complexes.

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[17] Using the steady-state approximation for $C_2O_4^-$, the integrated rate law for (1)–(3) is

$$\ln\left(\frac{[Co(C_2O_4)_3^{3-}]_0}{[Co(C_2O_4)_3^{3-}]_t}\right) - {}^1/_2 \ln\left(\frac{[Co(C_2O_4)_3^{3-}]_0 + (k_3/2k_2)[O_2]}{[Co(C_2O_4)_3^{3-}]_t + (k_3/2k_2)[O_2]}\right) = k_1 t$$

[18] We have verified this point at 35° and $[Co(C_2O_4)_3^{3-}] = 4 \times 10^{-3}$ *M* where the first-order plot is linear for >90% of reaction when the solution is continuously purged with N_2, while curvature begins after 78% in nondeaerated solution and after 66% when O_2 is bubbled through the solution continuously.

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A New Synthesis of 1,4,8,11-Tetraazacyclotetradecane (Cyclam) *via* the Nickel(II) Complex

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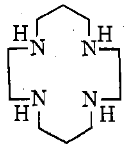
We wish to report a new synthesis of the title compound, I (hereafter cyclam). This ligand or the nickel complex which is the precursor may be obtained by the template synthesis outlined in the scheme of eq 1–3. This ligand is a highly desirable one for a variety of physical studies which require a complex with a planar array of donors and minimal steric requirements for



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