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]

	Obsd first-order rate constants, 10^5 sec^{-1} [b]		
$[Co(C_2O_4)_3^{3-}]_0$, *M*	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
$(3.99–2.41) \times 10^{-6}$	[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.

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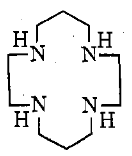
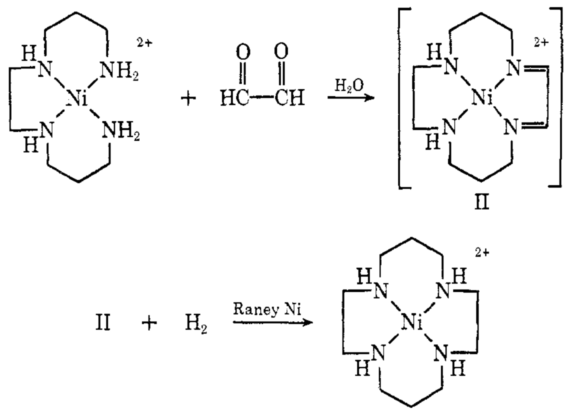
We wish to report a new synthesis of the title compound, I (hereafter cyclam). This ligand or the nickel complex which is the precursor may be obtained by the template synthesis outlined in the scheme of eq 1–3. This ligand is a highly desirable one for a variety of physical studies which require a complex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



I



$$\text{III} + \text{excess } CN^- \longrightarrow \text{I} \qquad (3)$$

the connecting organic linkages. The tetramine was first claimed by Van Alphen[1] and was then unambiguously synthesized by Stetter and Mayer[2] by a lengthy process (24% overall yield). Bosnich, *et al.*, used a modification of Van Alphen's procedure for synthesizing the ligand (*ca.* 5% yield) and prepared the first coordination complexes using this tetramine.[3] The present synthesis is a simple one and yields *ca.* 20% of the nickel complex or the free ligand.

Experimental Section

1,5,8,12-Tetraazadodecane, 3,2,3-tet, was prepared by the procedure given by Hamilton and Alexander.[4] The Raney nickel catalyst is Grace Chemical Co. Grade 28.

Preparation of Cyclam.—In a typical preparation (step 1) 26 g (0.15 mol) of 3,2,3-tet and an equivalent amount of $Ni(ClO_4)_2 \cdot 6H_2O$ (54.7 g) were dissolved in 600 ml of water to give a blue solution. The metal–ammine solution was cooled to *ca.* 5° and 24 ml of 40% aqueous glyoxal was added. The solution was stirred well and allowed to stand at room temperature overnight. In step 2 the solution was transferred to a bomb of sufficient volume along with several grams of Raney nickel and hydrogenated under 200–300 psi for 12 hr. In step 3 the catalyst was removed by filtration and 50 g of NaCN was added to the solution which was then heated at reflux for 2 hr. The solution was cooled and then extracted with several 50-ml portions of $CHCl_3$. These extracts were combined, dried with sodium sulfate, and evaporated to dryness. The yellowish solid which resulted was suspended in 100–150 ml of hot acetonitrile for 15–20 min. The suspension was cooled to room temperature and the solid was collected and washed with ether to yield *ca.* 6 g or a 20% yield of cyclam as fine white needles. This material was pure enough for most purposes but the material may be recrystallized from THF or dioxane if desired. *Anal.* Calcd for $C_{10}H_{24}N_4$: C, 59.96; H, 12.07; N, 27.97. Found: C, 59.42; H, 11.78; N, 27.57. The material has infrared and nmr spectra identical with those of cyclam prepared by Tobe's method.[3]

The reaction may be run on a smaller scale and hydrogenated at 50–60 psi using a Parr hydrogenation apparatus, sometimes with a slight reduction in yield.

Isolation of Ni(cyclam)$(ClO_4)_2$.—The nickel complex was isolated after step 2 by evaporation of the filtrate obtained after removal of the catalyst. Orange crystals were obtained after evaporation to *ca.* one-fourth the initial volume. The filtrate was evaporated until it was semisolid and was then taken up in hot water and stirred for a short time with charcoal. The mixture was filtered hot and the filtrate cooled. A second crop of orange crystals was obtained. Evaporation of the filtrate gave a third crop of material. The total yield of dried product was 21% of the theoretical value. All fractions were combined, recrystallized from hot water, and dried *in vacuo*. *Anal.* Calcd for $NiC_{10}H_{24}N_4Cl_2O_8$: C, 26.24; H, 5.29; N, 12.24; Ni, 12.83. Found: C, 26.66; H, 5.10; N, 12.10; Ni, 12.64. *Note!* According to the analyst this material explodes violently upon combustion.

Physical Measurements.—Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer Model 457 spectrophotometer. Nmr spectra were obtained on $CHCl_3$ solutions with a Varian A-60 spectrometer.

Results and Discussion

The reaction scheme utilized in this synthesis involves the well-known condensation of an α-diketone with a primary amine to yield an α-diimine which is stable to hydrolysis as a result of coordination to the metal ion. Such reactions are well known and this method has been used to prepare α-diimine bidentate[5] and tetradentate[6] ligands by condensation of an α-diketo reagent with the appropriate monoamine or diamine, respectively. More recently this method has led to cyclic ligands of the 14-membered type.[7] Much of the earlier work, especially the cyclization reactions, used 2,4-butanedione as the diketo reagent. In the case of cyclization reactions involving a metal template, condensations were successful only in the presence of dilute mineral acid. While conceptually the cyclam synthesis using glyoxal is identical, we were unable to obtain a reaction under these conditions. In aqueous solution, however, glyoxal reacts rapidly with the Ni(II) complex of 3,2,3-tet to yield an intermediate which is presumed to have structure II. Initial efforts to isolate this intermediate have been unsuccessful. Hydrogenation of the intermediate using Raney nickel catalyst yields Ni(cyclam)$^{2+}$ (III in the scheme) which may be isolated if desired. Treating the solution with excess cyanide without isolation of the metal complex leads to free cyclam. It should be noted that the order of addition in the first step is critical. No reaction with the metal ion is apparent even after several days if glyoxal is added to the amine before addition of the nickel salt. Also no cyclam was obtained when 2 equiv of 1,3-diaminopropane was substituted for the tetramine or when the tetramine reacted with glyoxal without addition of nickel ion.

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Reactions of Germyl- and Silylphosphines with Glyoxal

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The germyl- and silylphosphines $R_3MP(C_2H_5)_2$ (M = Ge, Si) give a dipolar 1,2 addition on the car-