TABLE III
THERMAL DATA

Ligand	H_R, kcal/mol	H_A, kcal/mol
Pyridine	24.0 ± 0.7	25.9 ± 0.3
β-Picoline	25.3 ± 0.8	20.2 ± 0.4
γ-Picoline	15.4 ± 0.9	17.1 ± 0.5

scanning calorimetric curves for the loss of adduct ligands are shown in Figure 3 for each of the adducts studied.

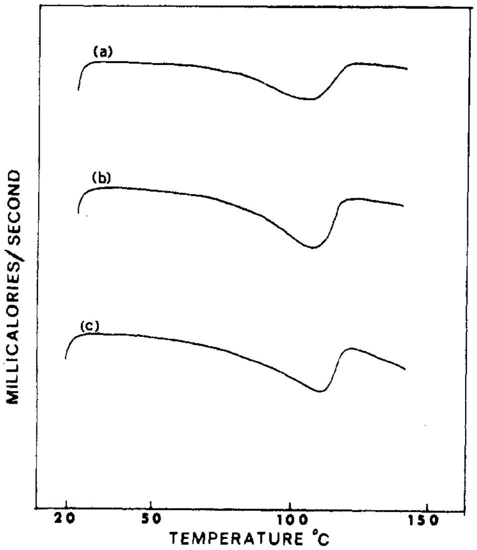

Figure 3.—Differential scanning calcrimetry curves for vaporization of the amine in (a) Ni(i-C_3H_7dtp)$_2$·2py, (b) Ni(i-C_3H_2dtp)$_2$·2β-pic, and (c) Ni(i-C_3H_7dtp)$_2$·2γ-pic.

The values for the pyridine and β-picoline adducts are comparable with values obtained by Beech and coworkers for the related NiL_4Cl_2 complexes. These workers found a value of 24.5 kcal/mol for the loss of two pyridine ligands and a value of 25.7 kcal/mol for the corresponding reaction with β-picoline.[31] The ΔH_R values are indicative of the expected trend in stability, that is, γ-picoline > β-picoline > pyridine, in agreement with the increased donor power of the nitrogen atom due to the substitution of the methyl group.

Sealed sample pans provided a means of obtaining latent heats of fusion of the Ni(i-C_3H_7dtp)$_2$ complexes, ΔH_A. These values are listed in Table III. The magnitude of the energy required to melt the crystals can be related to the compactness of the crystals. The ordering of the ΔH_A fusion energies, with a considerably larger value for the pyridine adduct, is in accordance with the less bulky character of pyridine as compared with the picolines.

Enthalpy values were also obtained for the purple Ni(i-C_3H_7dtp)$_2$ complex, $\Delta H = 10.1 \pm 0.5$ kcal/mol. This is in close agreement with the energy required to melt the residue from reaction 1 ($\Delta H = 10.5$ kcal/mol). We conclude from these values that the residue product was the starting complex Ni(i-C_3H_7dtp)$_2$.

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Induction of the Thallium(I)–Thallium(III) Exchange by Iron(II)[1]

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The oxidation of iron(II) by thallium(III) is believed to proceed *via* thallium(II) as an intermediate.[3] The thallium(I)–thallium(III) electron exchange is accelerated by irradiation with X-rays[4] and with ultraviolet light.[5] This effect has been ascribed to the formation of thallium(II) and rapid exchange reactions between this species and the 1+ and 3+ oxidation states. It is therefore to be expected that iron(II) will accelerate the thallium(I)–thallium(III) exchange. The present work was undertaken to investigate this possibility.

Experimental Section

Materials.—Baker Analyzed perchloric acid was used. Sodium perchlorate solutions were prepared from reagent grade sodium carbonate and perchloric acid. Thallous perchlorate was precipitated with perchloric acid from a solution of thallous nitrate and was recrystallized three times. A thallic perchlorate stock solution was prepared by anodic oxidation of thallous perchlorate. Iron(II) and iron(III) perchlorates were recrystallized from perchloric acid solution. The ^{204}Tl tracer, obtained in nitrate solution from Oak Ridge, was converted to thallous perchlorate with perchloric acid. Methyl isobutyl ketone (Eastman White Label) was passed through neutral alumina under argon immediately before use. Tributyl phosphate (Fisher Purified) and benzene (B & A reagent) were used without purification.

Procedure.—All runs were made in dark vessels, under argon, at 25°. Tracer was added in the form of a thallium(I)-204 perchlorate solution. In some runs the exchange was followed for about 1 hr before the addition of iron(II). Then iron(II) was added, and measurements were continued for several hours. In other runs, iron(II) was added 2 min before the tracer. The sequence of addition of iron(II) and tracer had no discernible effect on the results. Aliquots of the reaction mixture were removed at suitable time intervals and mixed with dilute hydrochloric acid. Thallium(III) was extracted, either with methyl isobutyl ketone or with a 20 vol % tributyl phosphate–benzene mixture. Liquid samples were counted in well-type sodium iodide scintillators, with circuitry adjusted for the Hg X-rays emitted in the decay of ^{204}Tl. In most runs both phases were counted. With the ketone extractant the organic-phase count was corrected for the slight extraction of thallium(I). With the tributyl phosphate–benzene mixture the thallium(I) was removed by backwashing with dilute hydrochloric acid before counting. An aliquot of the reaction mixture was counted without chemical separation. The counting rate per unit volume was multiplied by [Tl(III)]/([Tl(III)] + [Tl(I)]) to calculate x_∞, the "infinite time" counting rate of the thallium(III) fraction. Because [Fe^{II}] was always much less than [Tl^{III}], the variation of x_∞ during a run was small enough to be neglected. The exchange fraction F was taken as x/x_∞, where x is the counting rate of the thallium(III) fraction at time t.

Results and Discussion

The addition of iron(II) caused a marked increase in the rate of conversion of thallium(I) to thallium(III).

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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

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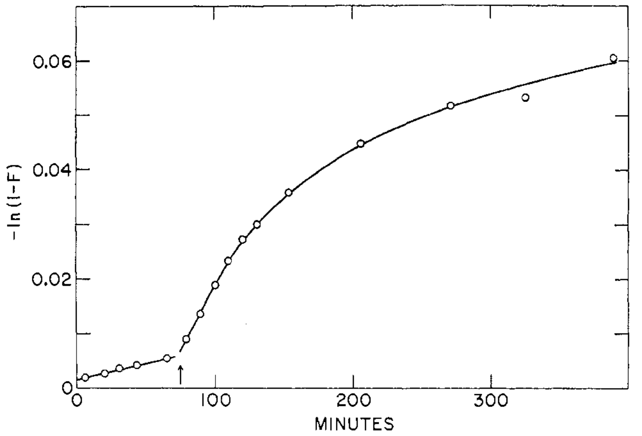

Figure 1.—Effect of ferrous ion on the thallous–thallic exchange. Conditions: $[\mathrm{Tl(III)}]_0 = 15.8 \times 10^{-3}\ M$; $[\mathrm{Tl(I)}]_0 = 0.44 \times 10^{-3}\ M$; $[\mathrm{Fe(II)}]_0 = 0.068 \times 10^{-3}\ M$, spiked at 75 min; $\mu = 3\ M$ (Na^+, H^+, ClO_4^-); $[H^+] = 0.67\ M$.

Representative results are given in Figure 1, which shows the increase with time of $-\ln(1 - F)$. Second-order rate coefficients were calculated by dividing the slopes of such plots by $(a + b)$. The values obtained for the interval before the ferrous spike agreed with literature values[6] of k_{ex} to within about 10% even though the extent of the exchange reaction was only about 1%. Values calculated from the slope of the nearly linear portion following the spike are taken as $k_{ex} + k_{acc}$, where k_{acc} represents the effect of ferrous ion on the exchange.

It was shown in separate experiments that the effect vanished when thallium(III) was omitted from the reaction mixture and also that variation of the radioactivity level by a factor 8 (from 4×10^3 dps/ml to 30×10^3 dps/ml) had no effect on the value of k_{acc}. It is therefore reasonable to infer that the effect is indeed an increased rate of exchange rather than a net oxidation of thallium(I) and that radiolytic reactions did not materially influence the results.

These results, obtained in perchlorate media, are in contrast to the observation of Challenger and Masters[4] that ferrous ion did not accelerate the exchange in 0.8 N H_2SO_4. The difference may lie in differences in the relative rates of reactions 1–5 in the two media.

A rate equation for the exchange in the presence of iron(II) can be derived by considering the reactions

$$\mathrm{Tl^{III}} + \mathrm{Fe^{II}} \rightleftharpoons \mathrm{Tl^{II}} + \mathrm{Fe^{III}} \quad (k_1, k_{-1}) \qquad (1)$$

$$\mathrm{Tl^{II}} + \mathrm{Fe^{II}} \rightleftharpoons \mathrm{Tl^{I}} + \mathrm{Fe^{III}} \quad (k_2) \qquad (2)$$

$$^{*}\mathrm{Tl^{I}} + \mathrm{Tl^{II}} \rightleftharpoons {}^{*}\mathrm{Tl^{II}} + \mathrm{Tl^{I}} \quad (k_{\mathrm{I}}) \qquad (3)$$

$$^{*}\mathrm{Tl^{II}} + \mathrm{Tl^{III}} \rightleftharpoons {}^{*}\mathrm{Tl^{III}} + \mathrm{Tl^{II}} \quad (k_{\mathrm{III}}) \qquad (4)$$

$$^{*}\mathrm{Tl^{I}} + \mathrm{Tl^{III}} \rightleftharpoons {}^{*}\mathrm{Tl^{III}} + \mathrm{Tl^{I}} \quad (k_{ex}) \qquad (5)$$

Reactions 1 and 2 are the accepted mechanism for the oxidation of iron(II) by thallium(III) in perchlorate media.[3] Reactions 3 and 4 were proposed to explain the X-ray-induced[4] and photoinduced[5] exchange reactions. Reaction 5 is the normal electron exchange, assumed here to be independent of (3) and (4).

Use of steady-state approximations for [Tl(II)], as in ref 3, and for [^{204}Tl(II)], as in ref 5a, leads to an explicit although complicated expression for d ln $(1 - F)/\mathrm{d}t$. When terms in [^{204}Tl(III)] and in [Fe(III)] are neglected, a simpler expression, appropriate to the initial stages of the accelerated reaction, is obtained. This result is

$$-\frac{\mathrm{d}\ln(1 - F)/\mathrm{d}t}{a + b} = k_{ex} + \left(\frac{k_1 a}{k_2}\right)\frac{k_{\mathrm{I}} k_{\mathrm{III}}}{k_{\mathrm{I}} b + k_{\mathrm{III}} a + k_2 x} \qquad (6)$$

where F is the fractional degree of exchange, and a, b, and x are the concentrations of thallium(III), thallium(I), and iron(II), respectively. The effect of iron(II), *i.e.*, k_{acc}, is the composite term following k_{ex} in (6). It is to be noted that the *rate* of exchange is obtained by multiplying either side of (6) by ab. The rate of the induced exchange is $k_{acc}ab$. The concentration of thallium(II) in the early stages of the reaction is k_1a/k_2; and the rate of the induced exchange will be seen from (6) to be equal to the rate of exchange between thallium(I) and thallium(II), $k_{\mathrm{I}}bc$, multiplied by a factor which expresses the probability that when a thallium leaves the 2+ state, it does so by exchange with thallium(III) rather than exchange with thallium(I) or reaction with iron(II).

Equation 6 does not apply when the concentration of iron(II) is zero, since the derivation assumes that a steady state in thallium(II) has been established by reactions 1 and 2. It should also be observed that at sufficiently low but finite [Fe(II)] (6) will not be expected to describe the induced exchange since additional reactions of thallium(II), *e.g.*, with itself or with impurities, will become competitive with reaction 2.

Table I lists values of k_{acc} obtained under various conditions in the present work. The trends observed in k_{acc} are in accord with those predicted on the basis of (6), *i.e.*, decrease as [Tl(I)] is increased; increase as [Tl(III)] is increased, and decrease as [Fe(II)] is increased. However, the magnitude of the observed variation of k_{acc} with [Tl(I)] requires k_{I} to be much greater than k_{III} if (6) is correct. This is incompatible with the result of Stranks and Yandell that $k_{\mathrm{I}}/k_{\mathrm{III}} = 0.5 \pm 0.2$.

TABLE I

RATE COEFFICIENTS FOR INDUCED EXCHANGE

$10^3[\mathrm{Tl(III)}]_0$, M	$10^3[\mathrm{Tl(I)}]_0$, M	$10^3[\mathrm{Fe(II)}]_0$, M	$10^5 k_{acc}$, $M^{-1}\ \mathrm{sec}^{-1}$
$\mu = 3\ M$ (Na^+, H^+, ClO_4^-), $[H^+] = 0.67\ M$[a]			
15.4	28.4	0.55	3.7
12.4	3.0	0.49	8.2
15.4	2.8	0.55	8.2
15.8	2.9	0.068	10.1
15.8	0.89	0.068	25.8
15.8	0.44	0.068	45.8
$\mu = 1.2\ M$, $[H^+] = 1.1\ M$[b]			
16.7	2.4	0.076	8.6
16.6	1.42	0.076	10.0
16.7	0.93	0.076	14.5
16.6	0.48	0.078	16.3
4.0	0.52	0.040	9.4
4.0	0.52	0.099	7.3
4.0	0.52	0.198	5.1
4.0	0.52	0.297	3.4

[a] Conditions under which the thallium(III)–iron(II) reaction has been studied.[3] Average k_{ex} found in present work $6.3 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$. *Cf.* 6.5×10^{-5} [6a] and $7.5 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$.[6b]
[b] Conditions under which the photochemical exchange was studied.[5] Average k_{ex} (present work) $12.9 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$. *Cf.* 12.7×10^{-5} [6b] and $11.4 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$.[6c]

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The discrepancy appears to be outside the errors involved in the present work, which are perhaps 10–20% in the overall rate coefficient ($k_{ex} + k_{acc}$). A reasonable inference is that the mechanism described by reactions 1–5 is correct as far as it goes but is incomplete. We hope that additional studies will clarify the matter and will lead to estimates of the individual rate constants k_{-1} and k_2 for the reactions of thallium(II) with iron(III) and iron(II), respectively.

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CONTRIBUTION FROM THE ARCO CHEMICAL COMPANY,
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Lability and Stereochemistry of Dioxobis(2,4-pentanedionato)molybdenum(VI)

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It is possible for the octahedral complex dioxobis(2,4-pentanedionato)molybdenum(VI) to exist in two geometrical configurations. In one, the complex would contain the two oxo groups in a cis configuration, in the other they would be in a trans arrangement (Figure 1).

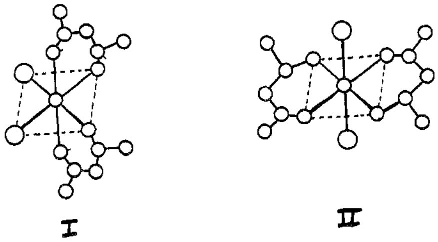

Figure 1.—(I) Cis isomer and (II) trans isomer.

The spectral properties characterizing these two alternative structures were discussed by Moore and Rice,[1] who concluded on the basis of infrared and nuclear magnetic resonance evidence that structure I was the correct assignment. We have verified this structure for the crystalline solid form of the compound by a complete three-dimensional X-ray diffraction study,[2] the main features of which are (a) the Mo–O bonds are shortest (1.69 Å) for the oxo ligands, (b) the two oxo ligands are mutually cis with an O–Mo–O angle of 105°, and (c) the Mo–O bonds to the two 2,4-pentanedionato oxygen atoms which are trans to the oxo ligands are longer (2.19 Å) than for the other two Mo–O bonds (1.98 Å). However, the variable-temperature nuclear magnetic resonance spectra (Figure 2) are indicative of considerable intramolecular lability in solution. We have observed the two methyl resonances ($\Delta\nu_{AB}$ = 2.35 Hz in benzene at 29° and $\Delta\nu_{AB}$ = 1.12 Hz in chloroform at 12°) and single ring proton resonance which Moore and Rice[1] claim characterize the cis configuration, but in addition, we have found that as the temperature is raised, the methyl resonances broaden and coalesce to a single line ($T_c(C_6H_6$ soln) = 313°K; $T_c(CHCl_3$ soln) = 290.7°K), while the ring proton resonance remains sharp.

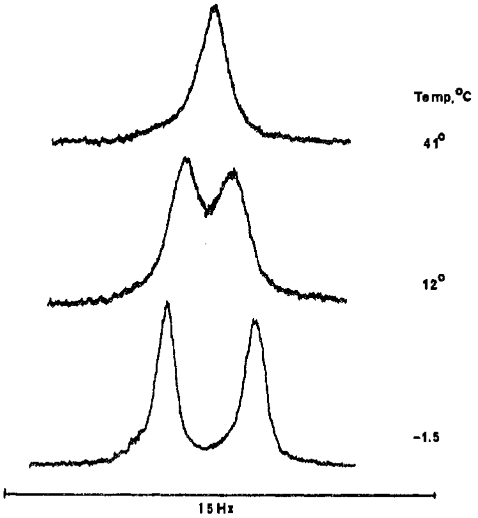

Figure 2.—The 100-MHz nmr spectra of dioxobis(2,4-pentanedionato)molybdenum(VI) in chloroform solution.

The stereochemistry of the complex permits two explanations of this observation: (a) the cis isomer, which possesses a twofold C_2 rotation axis and consequently has two nonequivalent sets of methyl groups, may be capable of rapid configurational changes which exchange the methyl groups between the nonequivalent sites; or (b) the cis isomer could be involved in a rapid equilibration with the trans isomer, which possesses magnetically equivalent methyl groups.

Experimental Section

Since dioxobis(2,4-pentanedionato)molybdenum(VI) appears to be readily hydrolyzed, particularly in solution, all handling was conducted under anhydrous conditions. Samples and solutions for physical measurements were prepared in an argon glove bag. The solvents, benzene and chloroform, were dried by refluxing for at least 12 hr over calcium hydride followed by distillation into bottles equipped with drying tubes. Acetonitrile (line width reference) was dried by refluxing over phosphorus(V) oxide and distilling. Dioxobis(2,4-pentanedionato)molybdenum(VI) was purchased from Research Organic/Inorganic Chemical Corp. and purified by vacuum sublimation. In spite of these precautions, the samples still showed evidence of decomposition; the benzene solution yielded a small yellow-white precipitate, while the chloroform solution which initially was a greenish yellow turned a deep blue after standing for 2 weeks. Proton nmr spectra were recorded with Varian A-60 and HA-100 spectrometers equipped with variable-temperature accessories. Problems of radiofrequency field saturation were encountered at the higher frequency and as a consequence the 60-MHz data are preferred. Temperature calibration was accomplished by measuring the chemical shift difference between the nonequivalent protons of ethylene glycol and methanol. The Varian ethylene glycol calibration was utilized in the case of the benzene solution spectra and the methanol calibration of Van Geet[3] for the chloroform solution spectra.

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