

The major evidence for the structural assignment for $\text{Cu}(\text{NO}_3)_4^{-2}$ is the spectral data. Magnetic data are not expected to differentiate between octahedral and tetrahedral arrangements. The low ϵ value for the maximum and the band position for the $\text{Cu}(\text{II})$ complex are in accord with those found for $\text{Cu}(\text{H}_2\text{O})_6^{+2}$.¹⁶ The observed intensity is very much lower than those observed for square planar $\text{Cu}(\text{II})$.

The infrared spectra indicate that the nitrate ion is coordinated in these ions. Free nitrate ion has D_{3h} symmetry. Upon coordination this symmetry is lowered to C_{2v} , causing a splitting of the ν_3 frequency (NO_2 asymmetric stretch) of the nitrate ion into a higher frequency, ν_4 (NO_2 asymmetric stretch), and a lower frequency, ν_1 (NO_2 symmetric stretch). The difference in wave numbers between ν_4 and ν_1 is reported to increase with an increase in the covalent contribution to the bonding. Application of this criterion to our data is not appropriate because the spectra were run on solids and the complexes contain bridging nitrate groups. A ν_2 frequency (NO stretch) which is inactive for ionic nitrate and a ν_6 frequency (non-

planar rock) also appear. A number of papers have appeared recently on the infrared spectra of free and coordinated nitrate.¹⁷⁻¹⁹ With the data now available, an unambiguous assignment of the symmetry of the nitrate group in most compounds can be made.

In Table III infrared spectral data are reported for the ions $[\text{Co}(\text{NO}_3)_4]^{-2}$, $[\text{Mn}(\text{NO}_3)_4]^{-2}$, $[\text{Ni}(\text{NO}_3)_4]^{-2}$, and $[\text{Cu}(\text{NO}_3)_4]^{-2}$. No bands occur which are assignable to free nitrate ion. The differences, $\nu_4 - \nu_1$, indicate that the nitrate is coordinated to the metal. It is interesting to compare these differences with the values of $\nu_4 - \nu_1$ found for $\text{Hg}(\text{NO}_3)_2$ (119 cm^{-1}), $\text{Zn}(\text{NO}_3)_2$ (200-250 cm^{-1}), $\text{Mn}(\text{NO}_3)_2$ (259 cm^{-1}), $\text{Cu}(\text{NO}_3)_2$ (250-300 cm^{-1}), $\text{K}_2[\text{Ce}(\text{NO}_3)_6]$ (244 cm^{-1}), and CH_3ONO_2 (385 cm^{-1}).^{7,18}

Acknowledgment.—The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

(17) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *Ibid.*, 4222 (1957).

(18) C. C. Addison and B. M. Gatehouse, *ibid.*, 613 (1960).

(19) J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **10**, 319 (1959).

(16) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

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Multidentate Ligand Kinetics. II. Zinc(II) and Ethylenediaminetetraacetatonickelate(II) with Copper(II) Catalysis

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The Zn^{+2} substitution reaction with nickel-EDTA¹ is $1/8500$ times as fast as the corresponding Cu^{+2} reaction at 25.0°. However, the same type of kinetic expression is found for Zn^{+2} and Cu^{+2} as contrasted to radionickel exchange and their relative rate constants permit the path of this type of substitution reaction to be characterized. A dinuclear reaction intermediate is proposed with an iminodiacetate segment of EDTA coordinated to the attacking metal ion. The catalysis of the Zn^{+2} reaction by traces of Cu^{+2} is studied.

Introduction

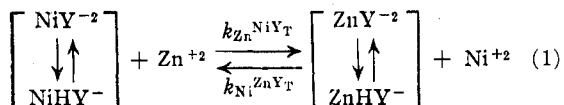
In a previous paper² the kinetics of the copper(II) reaction with the nickel-EDTA complex were shown to be quite different from the corresponding radionickel reaction. In this work zinc ion like nickel ion is found to be sluggish in

its attack on nickel-EDTA, but unlike nickel ion the zinc reaction is pH independent between pH 3 and 5. Thus, the kinetic dependence of the zinc ion is similar to that of copper ion. This permits their relative electrophilic ability to be related to the reaction intermediate (previously proposed) to determine which segments of EDTA initially bound to nickel are coordinated to the attacking metal ion.

(1) Ethylenediaminetetraacetic acid.

(2) T. J. Bydalek and D. W. Margerum, *J. Am. Chem. Soc.*, **83**, 4326 (1961).

The system studied is



where the acid forms of the complexes are in rapid equilibria. Correction must be made for the contribution of the acid dissociation reaction (indirect path to zinc-EDTA) in order to study the direct attack of Zn^{+2} on nickel-EDTA.

Experimental

The experimental procedures were similar to those reported previously.² As before, precautions were taken to avoid interference from other complexes or from trace impurities. The reaction system served as its own buffer and perchlorate salts were used throughout. The reaction was followed at the 380 m μ absorption band of nickel-EDTA, where the absorbances of zinc-EDTA and zinc ion were not appreciable. Zinc hydrolysis was not appreciable in the pH range studied.

The expression

$$\epsilon_{\text{NiYT}} = \frac{\epsilon_{\text{NiY}} + \epsilon_{\text{NiHY}}([\text{H}^+]/K_{\text{NiHY}})}{1 + [\text{H}^+]/K_{\text{NiHY}}}$$

was used for the apparent molar absorptivity, ϵ_{NiYT} , of the mixture of complexes at each pH. The values of ϵ_{NiY} , ϵ_{NiHY} , and ϵ_{Ni} are 11.2, 12.7, and 3.9, respectively, at 380 m μ .

The concentration of product in eq. 1 was

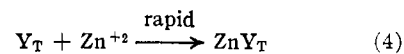
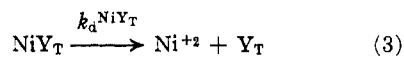
$$[\text{ZnYT}] = \frac{A_i - A}{b(\epsilon_{\text{NiYT}} - \epsilon_{\text{Ni}})}$$

where $[\text{ZnYT}]$ refers to the total concentration of the zinc complex at any time. The cell length b was 2 cm., A was the observed absorbance corrected for any background absorbance, and A_i was the initial absorbance of the reactants.

The nickel-EDTA complex has a greater stability ($K_{\text{NiY}} = 10^{18.6}$) than the zinc-EDTA complex ($K_{\text{ZnY}} = 10^{16.2}$) so that even with a large excess of Zn^{+2} the reaction in eq. 1 did not go far to the right. With zinc in large excess the forward reaction was pseudo first order in $[\text{NiYT}]$ and a first order $[\text{Zn}^{+2}]$ dependence was found with variation of the excess zinc. The equation

$$\log \frac{[\text{NiYT}]_i X_e + X([\text{NiYT}]_i - X_e)}{[\text{NiYT}]_i (X_e - X)} = \frac{(2[\text{NiYT}]_i - X_e)k_0 t}{2.303 X_e} \quad (2)$$

can be derived where X and X_e refer to the concentrations of ZnYT at time t and at equilibrium, respectively, and $[\text{NiYT}]_i$ is the initial concentration of the total nickel-EDTA. The term k_0 refers to total forward first order rate constant observed. Under the conditions used k_0 was equal to $k_{\text{Zn}^{2+}\text{NiY}_T}[\text{Zn}^{+2}] + k_{\text{d}^{\text{NiY}_T}}$. The $k_{\text{Zn}^{2+}\text{NiY}_T}$ term was constant because zinc was in excess. The $k_{\text{d}^{\text{NiY}_T}}$ term refers to the first order dissociation of nickel-EDTA which also leads to zinc-EDTA formation.



This constant is known from a radionickel exchange study³ so that correction could be made for the indirect path. By definition the indirect path is the path which is independent of the zinc ion concentration. The corrected rate constant, $k_{\text{Zn}^{2+}\text{NiY}_T}$, corresponds to the attack of zinc ion on the various forms of nickel-EDTA including the acid forms and therefore includes any possible combined zinc and hydrogen ion attack of nickel-EDTA.

Good linear plots were obtained for the left hand side of eq. 2 against time but due to the relatively small absorbance change and the consequent errors involved in the equilibrium measurement the rate constants were reproducible to only $\pm 10\%$.

The reactions were studied at an ionic strength of 1.25 M in order to compare them with previous work.

Results

Kinetics of the Zn^{+2} Reaction with NiYT .—

The acidity was varied from pH 4.9, where the direct attack accounted for 99% of the rate, to pH 3.05, where it accounted for only 40% of the rate. Below pH 3 the indirect path caused by acid dissociation so predominates that the direct zinc attack is difficult to measure. Reactions above pH 5 were avoided to eliminate any possible ZnOH^+ effect. Table I shows reproducible values for $k_{\text{Zn}^{2+}\text{NiY}_T}$ with variation in pH, $[\text{NiYT}]$, and $[\text{Zn}^{+2}]$ where

$$k_{\text{Zn}^{2+}\text{NiY}_T} = \frac{k_0 - k_{\text{d}^{\text{NiY}_T}}}{[\text{Zn}^{+2}]_i}$$

k_0 is obtained from plots of eq. 2 and $k_{\text{d}^{\text{NiY}_T}}$ corrects for the indirect reaction in eq. 3 and 4. The second order rate also can be expressed in terms of the individual nickel-EDTA species

$$k_{\text{Zn}^{2+}\text{NiY}_T}[\text{Zn}^{+2}][\text{NiYT}] = k_{\text{Zn}^{2+}\text{NiY}}[\text{Zn}^{+2}][\text{NiY}^{-2}] + k_{\text{Zn}^{2+}\text{NiHY}}[\text{Zn}^{+2}][\text{NiHY}^{-}]$$

It follows that

$$k_{\text{Zn}^{2+}\text{NiY}_T}(1 + ([\text{H}^+]/K_{\text{NiHY}})) = k_{\text{Zn}^{2+}\text{NiY}} + k_{\text{Zn}^{2+}\text{NiHY}}([\text{H}^+]/K_{\text{NiHY}})$$

and because $k_{\text{Zn}^{2+}\text{NiY}_T}$ is independent of $[\text{H}^+]$, both $k_{\text{Zn}^{2+}\text{NiY}}$ and $k_{\text{Zn}^{2+}\text{NiHY}}$ must be equal to $k_{\text{Zn}^{2+}\text{NiY}_T}$. This is analogous to the Cu^{+2} reaction, but the rate constants for Cu^{+2} are 6500 times larger.

Cu^{+2} Catalysis of the Zn^{+2} Reaction.—Since the Cu^{+2} reaction with nickel-EDTA was so much faster than the Zn^{+2} reaction, the possibility of a trace of Cu^{+2} catalyzing the Zn^{+2} reaction

(3) C. M. Cook, Jr., and F. A. Long, *J. Am. Chem. Soc.*, **80**, 33 (1958).

TABLE I
 RATE CONSTANTS FOR Zn^{+2} WITH NICKEL-EDTA

pH	$\mu = 1.25$	25.0°	
	$k_0,$ min. ⁻¹ $\times 10^6$	$k_d^{NiY_T},$ min. ⁻¹ $\times 10^6$	$k_{Zn}^{NiY_T},$ $M^{-1} \text{ min.}^{-1}$ $\times 10^4$
	$[Zn^{+2}]_i = 3.59 \times 10^{-1}, [NiY_T]_i = 1.59 \times 10^{-2}$		
4.90	5.6	0.06	1.5
4.32	6.2	.22	1.7
4.00	6.8	.54	1.7
3.40	7.7	2.69	1.4
	$[Zn^{+2}]_i = 3.59 \times 10^{-1}, [NiY_T]_i = 7.94 \times 10^{-3}$		
4.70	6.6	0.10	1.8
3.65	7.1	1.33	1.6
3.15	10.0	5.23	1.3
3.05	12.3	7.32	1.4
	$[Zn^{+2}]_i = 2.87 \times 10^{-1}, [NiY_T]_i = 7.94 \times 10^{-3}$		
4.80	5.4	0.08	1.8
4.15	4.4	.37	1.4

was investigated. The proposed catalysis was anticipated because other work in this Laboratory⁴ had shown that the Zn^{+2} attack on CuY^{-2} was rapid, permitting the sequence of reactions in eq. 5 and 6. When traces of copper ion were added to a reaction mixture, the observed rate of disappearance of nickel-EDTA increased greatly in proportion to the amount of copper added (Table II).

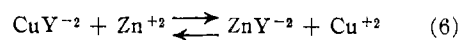
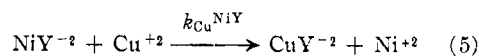
 TABLE II
 COPPER(II) CATALYSIS

$\mu = 1.25, 25.0^\circ, [NiY_T]_i = 0.0155, [Zn^{+2}]_i = 0.3945,$
pH 5.0

$[Cu^{+2}]$	$k_0, \text{min.}^{-1}$
1.34×10^{-6}	7.5×10^{-6}
5.36×10^{-6}	11.0×10^{-6}
1.34×10^{-4}	18.5×10^{-6}

The net disappearance of NiY^{-2} , if limited to the Cu^{+2} reaction in eq. 5, would be negligible, corresponding to only 0.1 to 1% of the reactant and would not be expected to shift the slope of the rate plot, but only its intercept. However, an accelerated rate is observed because the Cu^{+2} is rapidly regenerated by the reaction of the CuY^{-2} with Zn^{+2} (eq. 6). Thus, the Cu^{+2} is not consumed and because its reaction rate with NiY^{-2} is so much faster than Zn^{+2} very small amounts accelerate the loss of NiY^{-2} and the corresponding formation of ZnY^{-2} . Eventually, as the concentration of ZnY^{-2} increases, the equilibrium in eq. 6 shifts, reducing the amount of Cu^{+2} regenerated and therefore reducing the catalytic effect. Initial rates were studied before the tapering off of the catalytic Cu^{+2} role. These

rates encompassed a loss of NiY^{-2} concentration ten to one hundred times the amount of added Cu^{+2} .



The catalytic reaction was studied at pH 5.0 under conditions where the reverse reaction in eq. 6 was not important and gave rate constants dependent on trace concentrations of copper in accordance with eq. 7.

$$k_0 = k_{Zn}^{NiY} [Zn^{+2}]_i + k_{Cu}^{NiY} [Cu^{+2}]_i \quad (7)$$

A plot of k_0 against the initial copper ion concentration gave a straight line. The intercept gave a k_{Zn}^{NiY} value of $1.5 \times 10^{-4} M^{-1} \text{ min.}^{-1}$, in good agreement with the average value in Table I, and suggests a maximum impurity of 0.001% Cu^{+2} in the Zn^{+2} used. The slope gave a k_{Cu}^{NiY} value of $0.93 M^{-1} \text{ min.}^{-1}$, compared to the value of $0.98 M^{-1} \text{ min.}^{-1}$ reported previously.²

Kinetics of the Ni^{+2} Reaction with ZnY_T .

The reaction of Ni^{+2} with zinc-EDTA was studied in the presence of a large excess Zn^{+2} at pH values of 4.80 and 4.90. These conditions ensure that the reaction proceeds by the direct attack of Ni^{+2} on ZnY^{-2} rather than by Ni^{+2} and the free ligand. The system in eq. 1 is consistent in that the reverse reaction is first order in $[Ni^{+2}]_i$ and in $[ZnY_T]$. The average value for $k_{Ni}^{ZnY_T}$ was $4.0 \times 10^{-2} M^{-1} \text{ min.}^{-1}$ (see Table III). The equilibrium constant for eq. 1 calculated from the ratio of k_{Zn}^{NiY} to k_{Ni}^{ZnY} is 4.0×10^{-3} . This is in excellent agreement with the ratio of the stability constants for NiY^{-2} and ZnY^{-2} and with the average value of 4.2×10^{-3} which we determined spectrophotometrically.

This reaction also was studied at lower pH with only a small excess of Zn^{+2} . Under these conditions the Ni^{+2} reacts more readily with the free ligand in equilibrium with the ZnY_T . The desired rate is

$$\frac{d[NiY_T]}{dt} = k_{NiY_T} [Ni^{+2}] [Y_T] = k_{NiY_T} \frac{[Ni^{+2}] [ZnY_Y]}{K_{ZnY_T} [Zn^{+2}]}$$

where K_{ZnY_T} refers to the apparent stability constant of ZnY_T at the appropriate pH. Under conditions where the $[Ni^{+2}]$ was constant during the course of the reaction because of excess Ni^{+2} , the reaction was first order in $[ZnY_T]$ and inverse first order in $[Zn^{+2}]$. Some results are given in Table III. The value for k_{NiY_T} increases with pH as expected and agrees with other

(4) B. A. Zabin, Ph.D. Thesis, Purdue University, 1962.

values which can be calculated for this rate constant within the accuracy of the various stability constants.

TABLE III
RATE CONSTANTS FOR Ni^{+2} REACTION WITH ZINC-EDTA
 $\mu = 1.25$ 25.0°

pH	$[\text{Zn}^{+2}]_i$	$k_{\text{Ni}^{+2}\text{ZnY}_T}$
		$M^{-1} \text{ min.}^{-1}$
4.80	3.56×10^{-1}	4.1×10^{-2}
4.90	3.56×10^{-1}	3.9×10^{-2}
		$k_{\text{Ni}^{+2}\text{Y}_T}$
		$M^{-1} \text{ min.}^{-1}$
3.20	8.60×10^{-4}	1.08×10^4
3.35	8.60×10^{-4}	1.32×10^4

Discussion

The general kinetic expression for the reaction of Zn^{+2} with nickel-EDTA is the same as that for the reaction of Cu^{+2} with nickel-EDTA. In both systems the rate is not acid-catalyzed, that is, the hydrated metal ion reacts at substantially the same rate with NiY^{-2} and NiHY^- . The difference in the two systems is in the values of the rate constants, $0.98 M^{-1} \text{ min.}^{-1}$ for $k_{\text{Cu}^{+2}\text{NiY}}$ and only $1.5 \times 10^{-4} M^{-1} \text{ min.}^{-1}$ for $k_{\text{Zn}^{+2}\text{NiY}}$. Thus, Cu^{+2} is approximately 6500 times faster than Zn^{+2} in its reaction with NiY^{-2} . However, the mechanism proposed for the Cu^{+2} attack also can apply to the Zn^{+2} attack. In this mechanism a dinuclear reaction intermediate forms by partially unwrapping EDTA from nickel and coordinating it to the attacking metal ion. The transition state is then the breaking of one of the subsequent nickel-EDTA bonds. The lack of any significant kinetic effect for a 100-fold or greater change in hydrogen ion concentration means that any favorable proton participation in the reaction must be counterbalanced by an unfavorable role. Higher acidity might be expected to accelerate the dissociation of a dinuclear inter-

TABLE IV
RELATIVE STABILITY OF Cu^{+2} AND Zn^{+2} WITH SEGMENTS OF EDTA

Extent of unwrapping	Stability constants of free group ⁵	Relative stability		
		Cu^{+2}	Zn^{+2}	
One acetate	$\log K_1$	1.65	1.03	4.2
Two acetates	$\log \beta_2$	2.65
Glycinate	$\log K_1$	8.38	5.42	910
Iminodiacetate	$\log K_1$	10.55	7.03	3300

(5) J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants, Part I. Organic Ligands," The Chemical Society, London, 1957.

mediate, NiYM , but also would suppress its formation, so no net effect is observed. For very similar reaction paths with a reaction intermediate of the type NiYM , the relative effectiveness of Cu^{+2} and Zn^{+2} as M should correspond approximately to the relative stability of the EDTA segment which bonds these metal ions in the transition state. Table IV compares the stabilities which segments of an EDTA molecule would have with Cu^{+2} and Zn^{+2} . The right hand column of Table IV indicates that Cu^{+2} would be expected to be a more effective electrophilic agent than Zn^{+2} if they proceeded through the same intermediate and on an order of 3300 times if this intermediate involved an iminodiacetate complex forming with the attacking metal prior to the transition state. This is in good agreement with the observed value of 6500 corresponding to a total shift of only 0.3 log K unit between two stability constants. Any lesser degree of coordination to the attacking metal ion would not account for the effectiveness of Cu^{+2} compared to Zn^{+2} . On the other hand, an intermediate with a higher degree of coordination to Cu^{+2} than Zn^{+2} would give too large a ratio. Therefore, the proposed mechanism proceeds through an NiYM reaction intermediate with at least three EDTA dentates broken from the nickel ion and M^{+2} complexed by the iminodiacetate segment. The transition state involves subsequent breaking of nickel bonds. This mechanism does not specify how much additional unwrapping of Ni-EDTA occurs before the transition state. Other bonds may break but obviously some relatively slow cleavage from nickel must remain. Therefore a higher degree of coordination to the attacking metal ion before the transition state seems unlikely. This mechanism does suggest that any steric hindrance to unwrapping an iminodiacetate segment from the nickel ion would greatly retard the rate of metal ion attack. In fact, we will show in a subsequent paper that when a cyclohexene group bridges the nitrogen atoms instead of an ethylene group, there is no metal ion attack at all. Thus, 1,2-diaminocyclohexanetetraacetatonickel(II) has no copper(II) attack because its ring structure prevents the formation of an iminodiacetate type intermediate.

An attempt can be made to take into account the effect of charge on the relative stability of a polynuclear intermediate. A comparison of the relative stabilities of copper and zinc complexes with 2-di-(carboxymethyl)-aminoethyltrimethyl-

ammonium ion,⁵ $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$, gives a stability ratio of only 250. On the other hand, if the transition state involves the combined cleavage of the remaining chelates to nickel there may not be a high positive charge from nickel on the nitrogen atom which is adjacent to the iminodiacetate group bonded to copper (or zinc) and the iminodiacetate segment serves as a better model.

The mechanism suggests (1) that EDTA type complexes with any steric hindrance to unwrapping an iminodiacetate segment will be much less readily attacked by metal ions, (2) that the rate of attack of other labile ions will parallel the stability of their iminodiacetate complexes, (3) that metal ions having slower dentate transfer (Fe^{+3} , Ni^{+2} , etc.) will be much less effective, and (4)

that factors affecting slow dentate transfer (or water loss) will affect the reaction rate. The catalysis by traces of copper ion in the zinc-nickel-EDTA reaction is indicative of a vital kinetic consideration which could spoil other exchange studies, particularly for sluggish reactions where a labile contaminant is possible. This would include radiochemical exchange studies as well as other displacement reactions. Traces of other ligands also can catalyze multi-dentate exchange reactions.⁶

Acknowledgment.—The authors wish to thank the Air Force Office of Scientific Research for support of this research.

(6) D. C. Olson and D. W. Margerum, *J. Am. Chem. Soc.*, **84**, 680 (1962).

CONTRIBUTION FROM THE CLIMAX MOLYBDENUM COMPANY OF MICHIGAN RESEARCH LABORATORY, DETROIT, MICHIGAN

Synthesis and Properties of Molybdenum(III) Acetylacetonate

By MELVIN L. LARSON AND FRED W. MOORE

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Molybdenum(III) acetylacetonate, $\text{Mo}(\text{C}_5\text{H}_7\text{O}_2)_3$, was synthesized by three routes: reaction of acetylacetonone with an aqueous solution of potassium hexachloromolybdate(III), reaction of acetylacetonone with electrolytically-produced Mo^{3+} , and the reaction of $\text{Mo}(\text{CO})_6$ with refluxing acetylacetonone. It is sublimable, decomposes above its melting point (228–229°), and is monomeric in boiling benzene. Although it is non-reactive toward Lewis bases (water, benzophenone, pyridine, and triphenylphosphine), solvation in carbon tetrachloride causes replacement of one acetylacetonate group with chlorine. This new molybdenum acetylacetonate is reactive toward oxygen to yield a new, brown form of molybdenyl acetylacetonate, $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$.

Discussion

The chemistry of the acetylacetonates of molybdenum with an oxidation number of three is ill-defined. A molybdenum(III) acetylacetonate was synthesized by Morgan and Castell¹ from molybdenum oxychloride tetrahydrate, $\text{MoOCl}\cdot 4\text{H}_2\text{O}$, and acetylacetonone in aqueous alcohol. Brown crystals were obtained which analyzed as $\text{MoO}(\text{C}_5\text{H}_7\text{O}_2)\cdot 2.5\text{H}_2\text{O}$. This compound was attacked by air and was decomposed by dilute acids and alkali. The only other literature report was that of "molybdenum(III) acetylacetonate" in a report of some cell constants and paramagnetic resonance.^{2,3}

The only well established molybdenum acet. I-acetonate is the yellow molybdenyl acetylacetonate, $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, which is a derivative of the

MoO_2^{2+} cation. Unfortunately, this molybdenum(VI) acetylacetonate has limited solubility and is readily decomposed in solution.⁴ It was deemed advisable to attempt the synthesis of a hexacoördinate molybdenum(III) acetylacetonate because Mo^{3+} would have an ideal d^3 configuration for a stable octahedral structure, as predicted by the ligand-field theory.⁵ It also was hoped that this molybdenum(III) chelate

(1) G. T. Morgan and R. A. S. Castell, *J. Chem. Soc.*, 3252 (1928).

(2) H. S. Jarrett, *J. Chem. Phys.*, **27**, 1298 (1957).

(3) A recent private communication from Dr. J. C. Thomas, E. I. du Pont de Nemours and Company, reveals an independent synthesis of this compound by an electrolytic process.

(4) W. C. Fernelius, K. Terada, and B. E. Bryant, *Inorg. Syn.*, **6**, 147 (1960).

(5) L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," John Wiley & Sons, Inc., New York, N. Y., 1960.