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ELECTRONIC STRUCTURES AND BONDING IN
1,3-DITHIONATES OF NICKEL(II) AND RELATED COMPOUNDS

by

John Charles Cooper

A DISSERTATION

Presented to the Faculty of
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TITLE

ELECTRONIC STRUCTURES AND BONDING IN

1,3-DITHIONATES OF NICKEL(II) AND RELATED COMPOUNDS

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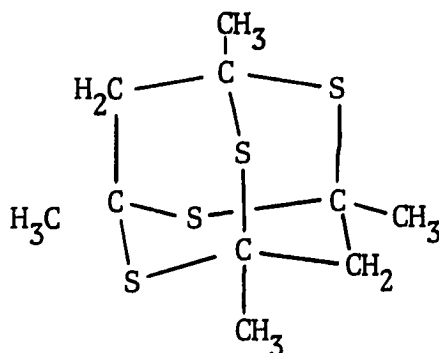
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INTRODUCTION

In recent years, metal complexes containing ligands with sulfur-donor groups have received much attention. Compared to oxygen donor ligands, the sulfur analogs usually result in complexes that are unusual and often quite different from the corresponding oxygen-containing complexes. The differences in stability and bonding are due presumably to the availability of d-orbitals in the outer electron shell of sulfur which can participate in π -bonding. The wide range of complexes formed by β -diketones has led to numerous attempts to prepare the sulfur-substituted analogs.

Although metal complexes of β -diketones have been known for more than seventy years,¹ the first sulfur analog was not reported until 1966, when Martin and Stewart² reported the synthesis of the dithioacetylacetonates of cobalt(II), nickel(II), palladium(II) and platinum(II). The dithioacetylacetonate ligand has never been isolated either as the anion or as the protonated ligand. It was only by performing the sulfur substitution in the presence of a transition metal ion that Martin and Stewart were able to isolate the complex.

Attempts were made as early as 1906³ to prepare dithioacetylacetone or other β -dithiones. Although the compound exists briefly in solution, the formation of the extremely stable dimer (I) is rapid and irreversible, and precludes isolation of the monomeric ligand either as a simple salt or in the protonated form. The structure of this product has been established by nuclear magnetic resonance spectroscopy and mass spectrometry.²



(I)

Because there has been no attempt to date to name the thio-derivatives systematically and because the dithio- β -diketones themselves cannot be isolated, the nomenclature of these compounds deserves specific attention. These problems are discussed and a systematic approach is described in Appendix I.

The first thio-substituted β -diketone complexes synthesized were of mono-thio-substituted ligands with nickel(II) by Chaston and Livingstone⁴ in 1964. Their method involved the isolation of the mono-thio-substituted β -diketone, then reaction with nickel acetate to form the complex, in a manner similar to the methods generally used to synthesize the β -diketone complexes.⁵ Since 1964, Livingstone and co-workers have synthesized a large number of similar complexes,⁶⁻¹⁶ with various substituents in the 1, 2 and 3 positions of the parent β -diketone. Other workers^{17,18} have prepared mono-thio derivatives by a slightly different method--a method similar to that used to prepare most of the dithio-substituted complexes. The parent β -diketone and a salt of the metal ion, usually the chloride, are dissolved in an alcohol, and hydrogen sulfide and hydrogen chloride are bubbled into the solution. Depending on the temperature, the rate of bubbling and the solvent used, sulfur is substituted in various degrees

into the final complex. This method has worked only for mono-thio derivatives of nickel(II). The mono-thio derivatives of other transition metals have generally been prepared by the first method, by first isolating the ligand.

All the mono-thio-substituted nickel(II) derivatives have been found to be diamagnetic. Because it is generally accepted that diamagnetic nickel(II) complexes have a square-planar geometry, these compounds have been assumed to be square-planar. This is consistent with the electronic spectra, and most interpretations of their infrared spectra have provided reasonably good correlations with expected electronic and physical properties, assuming a square-planar geometry.

The alternative is a tetrahedral structure similar to the structure of the bis(2,4-pentanedionato)nickel(II) complex in solution and would necessitate a paramagnetic species, based on the following argument. Figure 1 shows the d -orbital splitting expected for tetrahedral and square-planar coordination for complexes with mono-dentate ligands. It should be noted that in general, with the exception of the $d_{x^2-y^2}$ being the highest energy and the d_{xz} and d_{yz} having the same energy, the order of the orbitals in the square-planar case depends greatly on the particular metal ion and set of ligands involved; Figure 1 (b) is merely a representative case. In any event, since nickel(II) is a d^8 ion, in the tetrahedral case, maximum spin multiplicity in degenerate orbitals requires two unpaired electrons because the three highest orbitals are degenerate. However, in the case of the square-planar complex, if the separation of the $d_{x^2-y^2}$ orbital from the others is sufficiently great

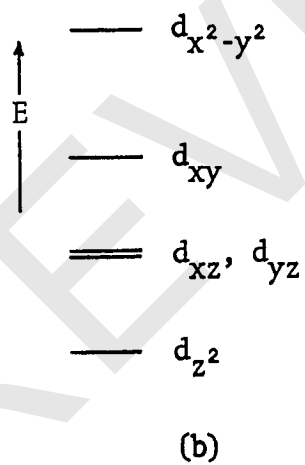
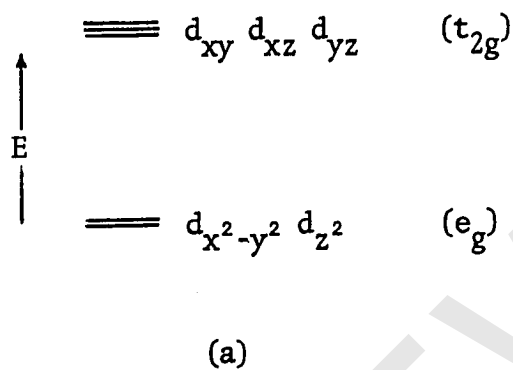


Figure 1. Expected d-orbital splitting in (a) a tetrahedrally coordinated and (b) a square-planar coordinated metal ion.

(that is, greater than the spin-pairing energy), then spin-pairing will occur, leaving the $d_{x^2-y^2}$ orbital vacant and a diamagnetic complex will result.

In the case of square-planar metal chelates (with D_{2h} symmetry, rather than D_{4h} as in the case of mono-dentate ligands), the decrease in symmetry and the increased possibility of overlap with ligand π orbitals results in changes in the order of the energy states and possible further splitting of degenerate orbitals.⁵ The d_{xy} and $d_{x^2-y^2}$ orbitals are reversed and there may be splitting of the degenerate d_{xz} and d_{yz} orbitals if they do not participate equally in π bonding.

In addition to the magnetic moment, the number and positions of the $d \rightarrow d$ transitions in the electronic spectrum can be used to determine the structure of the complex. Generally, in the case of the mono-thio derivatives of nickel(II), several $d \rightarrow d$ transitions are observed, consistent with a square-planar geometry. In the case of a tetrahedral complex, of course, the $d \rightarrow d$ transitions are degenerate and the energy of the transition is equal to $10dq$ (or Δ), the total ligand-field splitting of the d -orbitals.

One small problem that can arise in the interpretation of the electronic spectra, generally, of complexes containing sulfur-donor ligands is the possibility of mixing of the π molecular orbitals on the ligand with orbitals on the metal which are capable of π bonding (p_z , d_{xz} , and d_{yz} in the case of a square-planar complex.) In such a case, ligand field theory in its usual simple form may not be adequate and a more sophisticated molecular orbital treatment may be necessary. This problem will be

discussed later in connection with the electronic spectra of the square-planar dithio-substituted complexes.

The reason that the thio-substituted β -diketone complexes are square-planar and diamagnetic, unlike the corresponding β -diketonates, is probably due to the π -bonding ability of the sulfur atoms. Stabilization of the middle (up to the highest) molecular orbitals on the nickel by π -backbonding onto the sulfurs of the chelate rings should certainly favor the low spin configuration and thus the square-planar complex.

One very interesting aspect of the series of nickel(II) complexes with varying degrees of sulfur substitution is the possibility of polymer formation in the solid state and in solution by sulfur-to-metal or oxygen-to-metal bond formation. It has been demonstrated¹⁹ that bis(2,4-pentanedionato)nickel(II) has the structure shown in Figure 2, in the absence of water molecules to occupy the axial positions of the metal. A similar structure has been found for the cobalt(II) complex,²⁰ although it is actually a tetramer (rather than a trimer, as in the nickel(II) case). No such structures have been found for the dithio-substituted complex, in spite of the greater ability of sulfur to form such multiple bonds. The reason is probably the extreme stability of the monomer. However, the possibility of such polymer formation in solution has not been investigated. In addition, the mono-thio-substituted acetylacetonate of nickel(II), intermediate in this series, has never been thoroughly investigated except in very dilute solutions (electronic spectra) or in the solid state (infrared spectra and magnetic susceptibilities). An attempt to determine the extent of such possible polymer formation in solution was deemed worth-

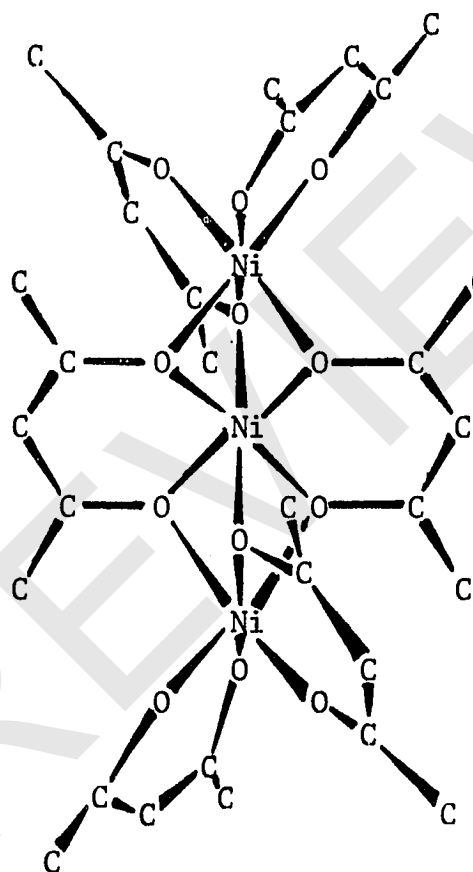


Figure 2. Structure of the nickel acetylacetonate trimer.

while. The nickel(II) complexes offer a particular advantage for such studies in that their diamagnetic character makes nmr a very valuable technique. One difficulty in studying the β -diketonates generally has been their paramagnetism in most cases, making nmr investigations difficult.

The first attempts to synthesize dithio-substituted complexes were of the acetylacetone derivatives and resulted in two types of compounds. The first was the type originally synthesized by Martin and Stewart.² The crystal structure was eventually determined for the cobalt(II)²¹ derivative and was found to be a square-planar monomer in the solid, very much as expected from other physical properties.

The second type of compound, however, was the iron(II) "complex"^{22,23}, which was found to contain four chlorines per metal atom. The structure of this compound has been variously formulated. Most of the proposed structures seemed to have little basis in experimental data or reason and involved bonding of chlorines to the chelate ring in the 1 and 3 positions and/or bonding of the chlorines to the metal. All the early structures involved coordination of the ligand to the iron in a more or less traditional manner. Knauer and co-workers, in their original article²² reporting the synthesis, suggested the correct structure but discarded it believing the intense color of the complex to be due to iron-sulfur bonding. The correct structure was revealed by Mason, et al.²⁴, who determined from the crystal structure that the compound was really bis(1,3-dimethyl-1,3-dithiolium) tetrachloroferrate(II) and by Heath, et al.²⁵, who reached the same conclusion based on electronic, infrared and Moessbauer spectra to-

gether with the temperature dependence of the magnetism of a series of such compounds.

The 1,3-dithiolium cation systems are very interesting from a synthetic standpoint, inasmuch as β -dithione complexes have recently been prepared from them by reduction in the presence of a suitable transition-metal ion.^{26,27,28} Campaigne and Hamilton²⁹ have written an excellent review article on the 1,3-dithiolium cation and related systems.

Most of the β -dithione complexes prepared have been with cobalt(II) or nickel(II). Although some complexes have been prepared with trivalent cations of iron, ruthenium and osmium,³⁰ and with cobalt, rhodium and iridium,³¹ these octahedral complexes are far less stable than the corresponding square-planar ones of the divalent cations. The stability increases with atomic number in a given family, however, and probably reflects some steric crowding of the six sulfur atoms about the small trivalent cations of the first transition series. Preparation of the complexes of trivalent cations varies, but usually involves the normal route in those cases where auto-oxidation does not occur. In the case of the unstable iron(III) complex of 2,4-pentanedithione, the synthesis is accomplished by reducing the bis(dithiolium) tetrachloroferrate(II) salt with a suitable reducing agent such as sodium borohydride or sodium dithionite.

The work discussed in this paper deals almost entirely with thio-substituted β -diketonates of cobalt(II) and nickel(II). These are the most stable, and little synthetic work or studies of physical properties has been done. Although Ouchi and co-workers³² have reported syntheses of several 1,3-substituted β -dithione complexes of this type, little in

the way of analysis of substituent effects or characterization of the products obtained is reported.

A large number of studies of the "pseudo-aromaticity" of metal keto-enolate rings has been done. In general, these compounds undergo many reactions characteristic of aromatic rings, and substituent effects are similar to those of aromatic systems. Unfortunately, determination of aromatic character from the chemical shifts of chelate-ring protons by nmr techniques is usually restricted to the keto-enol forms of the β -diketones themselves, because most of the metal complexes are paramagnetic.

In addition to providing diamagnetic complexes for study by nmr techniques, the nickel(II) β -dithionates provide the additional possibility of extension of the π system of the chelate ring through the metal ion to form a truly aromatic system. If π -delocalization does extend through the metal ion, it should be evident in the infrared spectra through substituent effects on the metal-sulfur bond and in the electronic spectra in the form of mixing of the d orbitals capable of π -bonding with the π molecular orbitals of the ligand. In addition, the proton nmr of both ring and substituent protons should be similar to that of aromatic systems.

In connection with the aromaticity of the chelate ring there is another problem which has not yet been satisfactorily solved. Lintvedt^{5,33} concluded, based on proton nmr of β -diketones with phenyl, 2-thienyl, and 2-furyl substituents in the 1 and 3 positions, that aromatic groups in these positions were coplanar with the enolic ring. This is consistent with the results of Rao and Mathur³⁴; based on thermochemical studies which showed an increase in free energy and enthalpy of ionization when a phenyl group was substituted for a methyl group, they concluded that the phenyl ring was

coplanar with the enolic ring, acting as an electron-donor through resonance. Similarly, Singh and Sahai found a shift to lower energy in all the $\pi \rightarrow \pi^*$ electronic absorption bands for the metal β -diketonates when the methyl groups were replaced by phenyls; this shift was interpreted as a dominance of the resonance effect over the weak induction effect of the phenyl. Although x-ray crystal structures of the γ -phenyl-substituted complex of copper(II) shows the phenyl ring and chelate ring to be nearly perpendicular (70°), this is most likely due to steric hinderance between the phenyl and the two methyls. The odd angle supports this reason inasmuch as there should be no electronic preference for this position. In any event, the other physical evidence available for the 3-phenyl-acetyl-acetone complexes support this structure in solution also. Finally, most infrared and polarographic data⁵ support a coplanar arrangement (both solution and solid state) for the copper chelates of 1,3-aromatic-substituted β -diketones and a non-coplanar structure for those substituted in the γ position.

There are, however, very convincing arguments to contradict this theory. Burdett and Rogers³⁷ have presented fairly convincing arguments that the stabilization of the enol forms of a phenyl-substituted (1 and 3 positions only) β -diketone is due to inductive electron withdrawal rather than electron delocalization. Sardella, et al.,³⁸ have presented the results of a very careful study of the proton nmr's of a series of para-substituted benzoylacetones. Their results indicate a fairly significant contribution to enol-stabilization from the trans-enol conformer, based on an analysis of the long-range couplings and the hydroxyl and substituent chemical shifts. Their findings, that the more electron-releasing groups on

the phenyl ring tend to stabilize the adjacent carbonyl group, leads to the conclusion that the enol stabilization of the phenyl ring is due to inductive effects of the phenyl ring. This would mean that the phenyl ring would probably not be coplanar with the enolic ring.

Supporting the inductive-effect theory are studies of the substituent effect on the acid dissociation constant, the infrared bands of $\nu(\text{C}\equiv\text{O})$ and $\nu(\text{C-H})$, and the UV band frequencies.³⁹ Although a linear relationship with Taft substituent σ^* constants was found, resulting in the conclusion that the inductive effect was most important, failure to take into account the combination nature of the $\nu(\text{C}\equiv\text{O})$ and $\nu(\text{C-H})$ infrared bands and failure to deconvolute the electronic bands to obtain accurate band positions make these results uncertain. (The term "deconvolution" as used here and as generally applied to electronic spectra, refers to the process of determining the exact positions, intensities, and widths of all the overlapping bands which contribute to the observed spectrum. The observed spectrum, at a given point, is the sum of the contributions from each band in the overlapping envelope. The process of deconvolution is simple and can be done without the use of computers if only two bands are involved. If several bands overlap, computer methods are essential. The details of the approach used in this work are discussed in Appendix II.)

However, Noskova and Zolotov⁴⁰ did a normal-coordinate analysis on some metal chelates of the 1,3-substituted β -diketones and, based on the C-H stretching bands, concluded that there was no π -electron delocalization, in the metal chelates, onto the metal ion. This, of course, seriously inhibits the resonance interpretation. The metal complexes would be expected to be more likely to exhibit π -electron delocalization onto the sub-

stituents than the parent β -diketones because of the greater availability of orbitals on the metal capable of π bonding than on the proton.

Finally, Noskova and Kazanova⁴¹ performed a molecular orbital calculation (using the L. C. A. O. method) for a variety of tris(β -diketone) complexes and bis(β -diketonato)zinc(II) complexes. Their results are in fair agreement with the experimental data. They found that the 1,3-substituents had little effect on the π bonding order of the chelates, but did affect the charge distribution. Their comparison was, however, based on published electronic spectra which were not deconvoluted, and used the L. C. A. O. method for calculating the molecular orbitals, which may be too simple an approach for these complexes.

One approach to solving this problem is to examine nmr data of the thio-substituted β -diketonates. The diamagnetism of the nickel(II) chelates makes them uniquely suited to this problem. In addition, having the chelate ring frozen in a planar position prevents the problems resulting from the presence of multiple species arising from keto-enol tautomerization, and should make the nmr spectra of the phenyl substituents easier to decipher.

One problem that must be considered in studying the nmr spectra of either metal β -diketonates or dithio- β -diketonates is the possibility of hydrogen-bonding of the deuteriochloroform to the complex and the effect this might have on the nmr resonances and on the electronic spectra. Deconvolution of the electronic spectra, analysis of the infrared spectra in various solvents to determine the mode of interaction (if any) of chloroform with these compounds, and studies of the nmr spectra in solvents other than deuteriochloroform should be considered a necessary part

of this work in view of the very substantial evidence in the literature^{42,43} for such solvent interactions for the β -diketonates.

One final problem involved in the study reported here is the mechanism involved in the synthesis of the dithio- β -diketonates. Mechanistic studies of the formation of these complexes would be very difficult to do in any quantitative way without very elaborate equipment and a large investment of time. The principal difficulty is the highly toxic nature of the hydrogen sulfide necessary for all present methods of synthesis. The necessity of using gases for reactants makes the situation even more complex.

Based entirely on experimental conditions needed, however, a fair idea of the mechanism involved can probably be obtained. It was expected, therefore, that this work would shed some light on the reaction path involved. The present published theories consist entirely of an acid-catalyzed substitution scheme, the most complete of which was suggested by Barraclough *et al.*¹⁸ The basic features of their proposed reaction scheme is shown in Figure 3. The scheme lacks detail because no quantitative attempts were made to establish this scheme. It is mostly well-founded speculation, and, as pointed out in their paper, the actual mechanism may be different for different metal ions, and, presumably, also may be different for parent β -diketones other than acetylacetone.

The reaction as shown in Figure 3 has been generalized to include other metal ions than nickel(II), because the inability to isolate incompletely-substituted complexes in the case of cobalt(II) is probably not sufficient reason to exclude it.

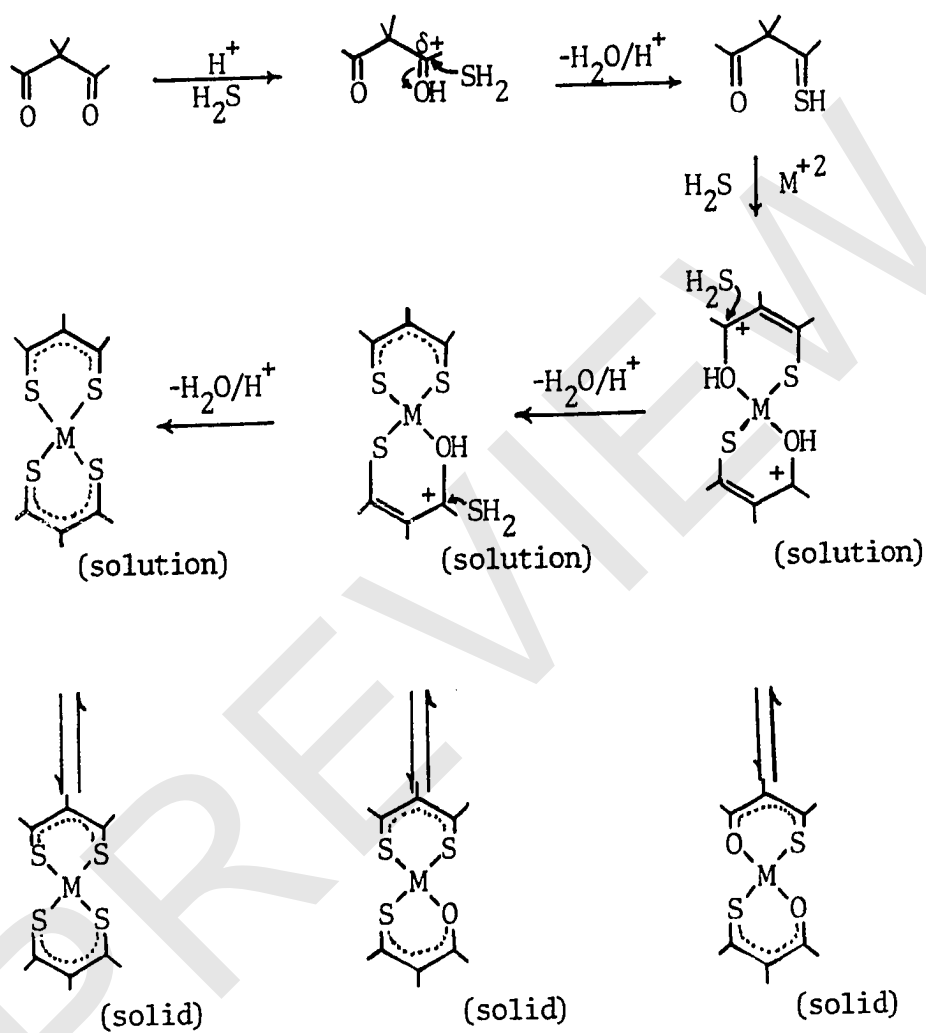


Figure 3. A possible over-all mechanism for formation of the thio-substituted β -diketone complexes.

In summary, the intent of this study includes several areas of investigation:

1. The synthesis of new complexes, particularly 1,3-substituted forms. If possible, the qualitative determination of the mechanism of formation.
2. A qualitative study of stabilities and bond strengths.
3. An analysis of the electronic characteristics of the chelate ring, including the extent of aromaticity.
4. The effect of substituents on stability and strength of the metal-sulfur bond.
5. A determination of the extent, if any, of intramolecular association of these compounds in solution.
6. An evaluation, if necessary, of the extent to which chloroform forms hydrogen bonds with, or otherwise forms adducts with, these compounds in solution.
7. The determination of the relative orientation in solution of the chelate ring and aromatic substituents.

Various physical methods are used in this study, including infrared, UV-visible, and nmr spectroscopy, and mass spectrometry. Most of the work reported in this paper involves the square-planar complexes of nickel(II) and cobalt(II) with dithio- β -diketones.

EXPERIMENTAL

I. Preparation and Sources of β -Diketones

In the syntheses of the 1,3-dithionates, it is necessary to prepare or purchase the parent β -diketones. Those that were prepared were prepared by a Claisen-type condensation using sodium amide as the basic condensing agent. This method has been adequately described elsewhere.^{5,44,45} A slight modification to the general procedure was the use of aqueous hydrogen chloride rather than acetic acid to acidify the initial water layer from the reaction mixture. This change eliminated problems of contamination of liquid products with acetic acid. The products were purified by vacuum distillation. The 1,3-diketones prepared in this way were 1-(p-methylphenyl)-1,3-butanedione, 5-methyl-2,4-hexanedione, 3,5-heptanedione, and 2,2,6,6-tetramethyl-3,5-heptanedione. Prepared by others⁴⁶ in this laboratory by different methods were 3-methyl-1,3-diphenyl-1,3-propanedione and 3,4-diacetyl-2,5-hexanedione.

Several β -diketones were obtained from commercial sources. The 2,4-hexanedione, 2,6-dimethyl-3,5-hexanedione, 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione and some of the 3,5-heptanedione and 2,2,6,6-tetramethyl-3,5-heptanedione were obtained from Eastman Organic Chemicals. The 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and the 1,1,1-trifluoro-2,4-pentanedione were obtained from Columbia Organic Chemicals, and the 2,4-pentanedione was from Fisher Scientific Company.

All the β -diketones used in this study were characterized by their nmr and infrared spectra, as well as melting points or boiling points, before use. In addition, the copper(II) chelates of most were prepared, and melting points and infrared spectra determined to confirm their identities.

II. Preparation of the thio-substituted β -Diketone Complexes

A. General Considerations -- There are several points in common to all the synthetic methods used in this study. With the exception of some of the bis(monothioacetylacetonato)nickel(II), all the thio-substituted complexes were prepared in situ by methods similar to those of Barraclough, et al.¹⁸

For reasons discussed later, solvents and starting materials were carefully dried before use. Methanol was reagent grade, from previously unopened pint bottles and was used without further purification. Ethanol was standard U.S.P. "100%" and was dried before use by distilling through a three-foot column of activated Linde 4 A molecular sieves and stored in dry pint bottles before use.

Hydrogen sulfide and hydrogen chloride were Matheson reagent grade and were dried by passing them through a two-foot by one inch gas-drying tube filled with Drierite during use. Because of the foul and very toxic nature of hydrogen sulfide and the excess amounts sometimes necessary in these preparations, the excess hydrogen sulfide was trapped as lead sulfide by passing the gases leaving the reaction flask through a saturated aqueous solution of lead acetate. A Drierite-filled drying tube was used