[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Infrared Absorption of Metal Chelate Compounds of 1,3-Diketones[1]

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RECEIVED FEBRUARY 11, 1957

The infrared spectra are described for thirteen 1,3-diketones, the copper chelates of seventeen 1,3-diketones, and the acetylacetone chelates of four metals.[2] Methods of preparation are described, including an improved method of preparing the copper chelates. The infrared spectra are discussed with respect to a comparison with spectra reported in the literature and to the relation of spectra to structure and stability. Assignments are made for several absorption frequencies.

Introduction

Two previous papers from this Laboratory[3,4] have described polarographic studies of copper chelates of 1,3-diketones. This paper presents studies of infrared spectra of several 1,3-diketones and their metal chelates.

A majority of the infrared work in this field, described thus far in the literature, concerns the chelates of acetylacetone with various metals,[5-11] including beryllium, magnesium, chromium, iron, cobalt, copper, zinc, thorium, uranium, nickel, aluminum, scandium, americium, samarium, boron-titanium and zirconium.

The amount of work on infrared spectra for metal chelates of other 1,3-diketones than acetylacetone is relatively small. Experimental studies have been reported for the copper chelates of thenoyltrifluoroacetone,[11] benzoylacetone,[11] dibenzoylmethane,[9,11] trifluoroacetylacetone[12] and hexafluoroacetylacetone.[12]

A few studies have been made of the infrared spectra of unchelated 1,3-diketones, including acetylacetone,[13] dibenzoylmethane,[13] and several fluorinated 1,3-diketones.[14]

The present paper describes preparation and infrared studies of thirteen 1,3-diketones, the copper chelates of seventeen 1,3-diketones, and the acetylacetone chelates of several metals.

Results and Discussion

The wave numbers of bands in the infrared spectra for the ligands and chelates studied are given in Tables I, III, IV and V.[2] Infrared intensity abbreviations used in the tables are: s, strong; m, medium; w, weak; b, broad; sh, shoulder. Bands in the Nujol region are not listed. Exact information on the origin of bands for metal coördination compounds is still relatively meager. Several of the assignments made in the tables and in the discussion, therefore, should be considered as tentative.

The following key to the Roman numeral designations used in Tables III, IV and V lists the ligand molecules

I. 3-Ethyl-2,4-pentanedione
II. 3-*n*-Propyl-2,4-pentanedione
III. 3-Chloro-2,4-pentanedione
IV. 3-Phenyl-2,4-pentanedione
V. 3-Benzyl-2,4-pentanedione
VI. Isovalerylacetone (6-methyl-2,4-heptanedione)
VII. Benzoylacetone (1-phenyl-1,3-butanedione)
VIII. Dibenzoylmethane (1,3-diphenyl-1,3-propanedione)
IX. 2-Furoyltrifluoroacetone [1-(2-furyl)-4,4,4-trifluoro-1,3-butanedione]
X. 2-Furoylperfluorobutyrylmethane [1-(2-furyl)-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione]
XI. 2-Thenoyltrifluoroacetone [1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione]
XII. 2-Thenoylperfluorobutyrylmethane [1-(2-thienyl)-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione]
XIII. 3-Bromo-2,4-pentanedione
XIV. 3-Iodo-2,4-pentanedione
XV. 3-Methyl-2,4-pentanedione
XVI. Trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione)
XVII. Hexafluoroacetylacetone (1,1,1,5,5,5-hexafluoro-2,4-pentanedione)

Metal Chelates of Acetylacetone.—The infrared spectra of the acetylacetone (2,4-pentanedione) chelates of copper(II), palladium(II), nickel(II), cobalt(II), manganese(II), magnesium(II), cadmium(II), aluminum(III), chromium(III), iron(III) and sodium(I) were determined. Of the 11, only the four not previously reported in the literature (palladium, manganese, cadmium and sodium) are listed in Table I.[2]

Although the spectrum of acetylacetone contains no intense bands in the 1500 cm.$^{-1}$ region, metal chelates of acetylacetone do absorb strongly in this region. Following the assigment of Lecompte,[5] the uppermost band is assigned to a perturbed (or chelated) carbonyl and the lower band to a perturbed carbon–carbon double bond. In the conjugated chelate ring, the carbonyl and carbon–carbon double bonds have less double bond character and more single bond character, accounting for

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(1) Abstracted from the M.S. Thesis of James P. Collman, June, 1956, University of Nebraska.

(2) Tables I, III, IV and V, containing the spectra referred to in the body of this paper, have been deposited as Document number 5129 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(3) H. F. Holtzclaw, Jr., K. W. R. Johnson and F. W. Hengeveld, THIS JOURNAL, **74**, 3776 (1952).

(4) H. F. Holtzclaw, Jr., A. H. Carlson and J. P. Collman, *ibid.*, **78**, 1838 (1956).

(5) J. Lecompte, *Disc. Faraday Soc.*, **9**, 125 (1950).

(6) C. Duval, R. Freymann and J. Lecompte, *Compt. rend.*, **231**, 272 (1950); *Bull. soc. chim. France*, 106 (1952).

(7) H. W. Morgan, U. S. Atomic Energy Commission Document No. 2659 (1949).

(8) B. P. Susz and I. Cooke, *Helv. Chim. Acta*, **37**, 1273 (1954).

(9) D. N. Shigorin, *Izvest. Akad. Nauk. S.S.S.R., Ser. Fiz.*, **17**, 596 (1953) [*C. A.*, **48**, 5651h (1954)]; *Zhur. Fiz. Khim.*, **27**, 554 (1953); [*C. A.*, **48**, 7478*i* (1954)].

(10) L. J. Bellamy, G. S. Spicer and J. D. H. Strickland, *J. Chem. Soc.*, 4653 (1952).

(11) L. J. Bellamy and R. F. Branch, *ibid.*, 4491 (1954).

(12) R. L. Belford, A. E. Martell and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

(13) R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

(14) J. D. Park, H. A. Brown and J. R. Lacher, *ibid.*, **75**, 4753 (1953).

the large frequency shifts of the carbon–carbon double bond adsorption band and the carbonyl absorption band upon chelation.

The position of the perturbed carbonyl band, usually the strongest band found in the spectrum of a given chelate, is perhaps largely dependent upon three factors: (1) the masses of the groups attached, at the ends of the ligand molecule, to the carbonyl groups, (2) interaction of the carbonyl with neighboring π or d-orbitals, and (3) the relative electron density of the σ bonds. The latter factor is, for the most part, controlled by the electronegativity of the groups attached to the carbon atom of the carbonyl group. For chelates of different metals but the same ligand, the mass effect probably has very little relation to the strength of the metal–oxygen bond. If more conjugation between the metal ion and the carbonyl exists in one metal acetylacetonate than another, this might be expected to result in a stronger metal–oxygen bond, less double bond character in the carbonyl group, and a lowering of the frequency of the perturbed carbonyl band.

Previous attempts to find a band or bands related to the stability of the chelates have met with only partial success. Bellamy and Branch[11] found that for bivalent metal complexes of salicylaldehyde, the shift of the carbonyl band followed the usual order of stabilities. A rough measure of stability was obtained from the positions of this band with bivalent metal chelates of 2-thenoyltrifluoroacetone. They reported, however, that there was no apparent relation between chelate stability and position of the carbonyl band for the bivalent metal chelates of acetylacetone.

The bands selected by Bellamy and Branch appear to have been, in each case, the most intense band found in the 1500 cm.$^{-1}$ region rather than the first or uppermost band in each case. Selection of the uppermost of the two bands seems to yield a significant relationship. The uppermost band in this region, from the spectra measured in the present work, is listed for several metals in Table II in order of decreasing frequency.

Van Uitert, Fernelius and Douglas,[15] from stability constants calculated from *p*H measurements, have reported the order of increasing stability of several metal chelates of acetylacetone to be: Mg(II) < Cd(II) < Mn(II) < Co(II) < Zn(II) < Ni(II) < Cu(II).

TABLE II

FREQUENCIES OF PERTURBED CARBONYL BANDS IN ACETYLACETONE CHELATES OF SEVERAL METALS

Metal	Frequency, cm.$^{-1}$	Metal	Frequency, cm.$^{-1}$
Na(I)	1630	Mn(II)	1607
Ni(II)	1618	Co(II)	1595
Mg(II)	1615	Cu(II)	1580
Cd(II)	1613	Pd(II)	1577

A comparison of these two series indicates, with nickel an exception, a qualitative relationship between the strength of the metal–oxygen bond, as obtained from the stability constants, and the frequency of the perturbed carbonyl absorptions. The position of palladium is reasonable on the basis of the order of stability reported by Mellor and Maley[16] for the salicylaldehyde chelates of several metals: Mg < Cd < Zn < Co < Pb < Ni < Cu < Pd.

Sodium acetylacetonate, essentially ionic, would be expected to have the least interaction between the metal and the carbonyl grouping and appears to fall in logical relationship to the chelates of the other metals. It is included in the list in Table II, therefore, although it is the only compound of a monovalent metal listed. The spectrum of sodium acetylacetonate probably can be considered as that of the acetylacetonate ion.

Various 1,3-Diketones and Copper Chelates.—Tables III, IV and V[2] list the spectra for the ligands I—XII, inclusive, and for the copper chelates of ligands I–XVII, inclusive. Agreement between the spectra reported in Tables III, IV and V and the few reported in the current literature is good. The spectra of pure liquid acetylacetone and of the copper chelates of trifluoroacetylacetone and hexafluoroacetylacetone agree, for most frequencies, within 0–3 cm.$^{-1}$ with values reported by Belford, Martell and Calvin.[12] The perturbed carbonyl bands for the copper chelates of 2-thenoyltrifluoroacetone and 1-phenyl-1,3-butanedione correspond closely with the values reported by Bellamy and Branch,[11] but that for the copper chelate of dibenzoylmethane (1552 cm.$^{-1}$) does not agree with the value of Bellamy (1524 cm.$^{-1}$). The discrepancy may be explained by the choice of the most intense band by Bellamy rather than the first strong band in the 1500 cm.$^{-1}$ region. Some other values reported by Bellamy vary a few wave numbers from those reported in this work. These differences are thought to be accounted for by the use of dilute chloroform solution by Bellamy, whereas Nujol suspensions were used in the present work. Bellamy reports a free carbonyl band for benzoylacetone which was not found in this work. His spectrum of dibenzoylmethane agrees with that reported in Table IV.

4000-1650 Cm.$^{-1}$ Region.—Very few copper chelates of 1,3-diketones absorb in this region. The origin of the weak absorption bands for the copper chelates of 2-thenoyltrifluoroacetone and 2-furoylperfluorobutyrylmethane at 3110 and 3140 cm.$^{-1}$, respectively, and the moderate band for the copper chelate of hexafluoroacetylacetone at 3550 cm.$^{-1}$ is uncertain.

Seven out of the thirteen 1,3-diketones examined show one or more hydroxyl bands in the 3600 to 3000 cm.$^{-1}$ region. The diketones in which such bands are not found may perhaps have absorptions in this region which are weak or poorly resolved. The molecules containing electronegative groups such as trifluoromethyl or perfluoropropyl are found to have hydroxyl bands at a lower frequency than the other 1,3-diketones in agreement with Belford, who in a recent study of fluorinated copper chelates[12] attributed the lowering of the hydroxyl frequency to the presence of a more acidic hydrogen.

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(15) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, THIS JOURNAL, **75**, 2736 (1953).

(16) D. P. Mellor and L. Maley, *Nature*, **159**, 370 (1947).

These bands are not sharp enough to provide more quantitative information about the acidity.

The next important absorption bands are the sharp, usually strong bands thought to be caused by free carbonyl absorptions of the keto form of the 1,3-diketone. These bands, present in the spectra of six of the thirteen diketones studied, disappear upon chelation. Except for 3-chloro-2,4-pentanedione, which has only one band centered at about 1725 cm.$^{-1}$, the diketones exhibit two such bands, one centered around 1700 cm.$^{-1}$ and the other around 1725 cm.$^{-1}$.

1650 to 1500 Cm.$^{-1}$ Region.—A strong, usually broad, band around 1610 cm.$^{-1}$, which disappears upon chelation, was observed in all of the diketones studied. The position of this band, which is characteristic of 1,3-diketones and which has been referred to as the "enol-chelate" band by Bellamy and Beecher,[17] does not seem to be related to the inductive or resonance effects of the group attached to the hydrogen-bonded, six-membered ring of the enol form.

The most important chelate band is the perturbed carbonyl band, usually the first strong band found in the spectrum of a copper chelate of a 1,3-diketone and ordinarily located around 1580 cm.$^{-1}$. In 11 of the 12 copper chelates for which the free diketone is also reported, the perturbed carbonyl bands of the chelate are at a lower frequency than the hydrogen-bonded carbonyl (enol chelate) band of the unchelated ligand. An exception is the copper chelate of 2-furoylperfluorobutyrylmethane, in which there are three bands which might conceivably be assigned to the perturbed carbonyl absorption, 1615 cm.$^{-1}$, 1598 cm.$^{-1}$ and 1580 cm.$^{-1}$. The 1598 band is probably caused by absorption of the furan ring. The 1615 band has been arbitrarily designated as the perturbed carbonyl band, because it is the first strong absorption and is higher than the expected furan absorption. The two bands at 1615 and 1598 cm.$^{-1}$ may, alternatively, both arise from furan absorptions, with the strong band at 1580 cm.$^{-1}$ originating from the chelated carbonyl group.

In contrast to the acetylacetonates of the various metals reported above, a comparison of the perturbed carbonyl bands of the copper chelates of the seventeen 1,3-diketones shows no apparent relationship to the stability of the chelates. Neither does the difference between the enol–chelate band of the ligand and the perturbed carbonyl band of the chelate, nor the difference between the perturbed carbonyl band and the perturbed carbon–carbon double bond, seem to have a direct relation to stability of the metal chelate. The absence of a relationship is not entirely unexpected. In comparing the acetylacetonates of various metals, the action of the ligand is essentially the same in each case and, except for the differences in the masses of the metals, any effect which strengthens the metal–oxygen bond weakens the carbon–oxygen carbonyl bond. For the copper chelates of various 1,3-diketones, on the other hand, the differences in resonance, inductive, and mass effects between the various chelates must be attributed essentially all to the ligand, the metal remaining the same, and may differ in their relative effects upon the metal–oxygen bond and the carbonyl bond. For example, a phenyl group attached to a carbonyl group in the ligand might set up an interfering conjugation through a quinoid-like structure, thereby decreasing the double bond character of the adjacent carbonyl group, lowering the frequency of the perturbed carbonyl band, and decreasing the strength of the copper–oxygen bond. This is illustrated by the spectrum of bis-(1-phenyl-1,3-butanediono)-copper(II), which has a perturbed carbonyl band at 1561 cm.$^{-1}$, compared to 1580 cm.$^{-1}$ for bis-(2,4-pentanediono)-copper(II) which is known to have a stronger copper–oxygen bond.[4] On the other hand, strong electronegative groups attached to the chelate ring cause a decrease in the stability of the chelate[4] but an increase in the strength of the carbon–oxygen carbonyl bond and therefore an increase in the frequency of the perturbed carbonyl absorption band. This is exemplified by bis-(hexafluoroacetylacetone)-copper(II) in which there are two strong bands at 1645 and 1615 cm.$^{-1}$ (either or both of which could be perturbed carbonyl absorptions). The increase in the first strong absorption band of the spectra of fluorinated copper chelates may be caused by the electron-attracting group increasing the force constant of the carbonyl bond.

Further, if a group capable of acting as an electron sink through resonance were attached to one of the carbonyls of a 1,3-diketone, and a strongly electronegative group were attached to the other carbonyl, the spectrum of the resulting chelate might contain two different perturbed carbonyl absorptions. The 1608 and 1568 cm.$^{-1}$ bands of bis-(2-furoyltrifluoroacetono)-copper(II) and the 1615 and 1580 cm.$^{-1}$ bands of bis-(2-furoylperfluorobutyrylmethane)-copper(II) may be explained in this manner. The analogous 2-thenoyl compounds are complicated by the presence of thiophene bands which may be at the same frequency as the second perturbed carbonyl band. In the furan-containing compounds, three bands were found, one of which logically is assigned to the furan ring.

The perturbed carbonyl band seems to be at a lower frequency for each of the copper chelates in which the carbon between the two carbonyl groups is substituted. This may be in part a mass effect. Although the information concerning mass effects upon absorption bands is meager at present, it is interesting to note that for chelates of 3-substituted 2,4-pentanedione a comparison of perturbed carbonyl frequencies with the masses of the substituted groups produces a reasonably good inverse relationship

Substituted group	Relative mass of group	Frequency of perturbed carbonyl
(Hydrogen)	1	1580
Methyl	15	1580
Ethyl	30	1577
Chloro	35.5	1571
n-Propyl	43	1577
Phenyl	77	1575
Bromo	80	1558
Benzyl	91	1570
Iodo	127	1547

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[17] L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 4487 (1954).

The additional factor of positive inductive effect of groups such as benzyl further complicates the factors controlling the position of the perturbed carbonyl absorption band.

Other bands in the 1650 to 1500 cm.$^{-1}$ region in either the free ligand or the chelate can be attributed to vibrations of functional groups, such as phenyl, furan and thiophene rings.

1500-800 Cm.$^{-1}$ Region.—A band centered around 1425 cm.$^{-1}$ in many of the 1,3-diketones and their chelates is probably caused by a methyl deformation. Similar assignments have been given by other workers, including Belford, Martell and Calvin[12] who have assigned the 1425 cm.$^{-1}$ band in acetylacetone to a methyl deformation. The compounds which have no methyl group substituted in the chelate ring fail to absorb in the 1425 cm.$^{-1}$ region.

Strong carbon–fluorine bands appear from 1300 to 1000 cm.$^{-1}$.

A range of additional perturbed carbonyl absorption has been reported by Lecompte[5] and by Bellamy and Branch[11] in the 1400 to 1300 cm.$^{-1}$ region. A comparison of several of the ligand and chelate spectra studied in the present work reveals a band which could, perhaps, be an additional perturbed carbonyl.

800–650 Cm.$^{-1}$ Region.—Strong bands occur in the upper 700 cm.$^{-1}$ region in the 1,3-diketones and their metal chelates. Ueno and Martell[18] ascribe similar bands in the range 779 to 740 cm.$^{-1}$ for metal chelates of bisacetylacetone–ethylenediimine and related compounds to C–H out-of-plane deformation vibrations. In compounds of the type $R'R''C{=}CHCH_3$, such vibrations are usually in the range 840-800 cm.$^{-1}$. Ueno and Martell reasoned that the aromatic nature of the six-membered hydrogen-bonded ring of the enol form of the ligand or of the conjugated chelate ring explains the lowering of these absorptions.

The 1,3-diketones which are substituted at the methylene carbon between the two carbonyl groups could have no hydrogen on the carbon–carbon double bond of the ligand enol form nor on the carbon–carbon double bond of the chelated ligand. The spectra of the chelates and free ligands are listed in Table III for compounds in which ethyl, *n*-propyl, chloro, phenyl and benzyl groups have been substituted at the number three carbon of 2,4-pentanedione. In Table V, the spectra of chelates are listed in which bromo, iodo and methyl groups have been substituted. The spectra of several of these ligands and chelates show bands in the 700 cm.$^{-1}$ region which cannot be attributed to a hydrogen out-of-plane deformation. The origin of this absorption is the more puzzling, inasmuch as the absorption band, in agreement with the observations of Ueno and Martell for the ethylenediimine compounds, seems to be almost unaffected by chelation of the ligand or by drastic alteration of the metal used in chelating the ligand.

Below 700 cm.$^{-1}$, absorption bands are expected which are caused by metal–oxygen vibrations.[5] Such bands, however, are conspicuously absent down to 650 cm.$^{-1}$ in most of the spectra of copper chelates of 1,3-diketones studied in the present work. In only a few instances (the copper chelates of 2,4-pentanedione, isovalerylacetone, 3-benzyl-2,4-pentanedione and 3-*n*-propyl-2,4-pentanedione) were bands found in this region which could be so assigned after comparing the spectra of the chelate and of the corresponding free 1,3-diketone. The possibility exists that an examination of the frequency region below 650 cm.$^{-1}$ might reveal additional bands which could be assigned to metal–oxygen vibrations.

Acknowledgment.—The authors wish to thank the Research Council of the University of Nebraska for a grant which partially supported this investigation.

Experimental

Spectra.—All spectra were determined in the frequency range 4000-650 cm.$^{-1}$ with a Perkin–Elmer Model 21 recording spectrophotometer, using sodium chloride optics.[19] Compounds usually were examined as solids in Nujol mulls. A few samples, as indicated in the tables, were studied as pure liquid films.

Preparation and Purification of Compounds. Metal Chelates.—1. The acetylacetonates of palladium(II), manganese(II) and cadmium(II) were prepared and analyzed by Wenz.[20] The copper chelates of hexafluoroacetylacetone and trifluoroacetylacetone were obtained from Professor A. L. Henne of The Ohio State University. Preparation and analysis of the copper chelates of acetylacetone, 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, 3-methyl-2,4-pentanedione, 3-ethyl-2,4-pentanedione, 3-*n*-propyl-2,4-pentanedione and 3-phenyl-2,4-pentanedione and the respective ligands are described in previous articles.[3,4]

2. **Sodium Acetylacetonate.**—The method of Morgan and Rawson[21] was used. The white precipitate was filtered, washed successively with cold, absolute ethanol and cold ether, dried and weighed; yield 23.0 g. (78%).

3. **Bis-(isovalerylacetono)-copper(II).**—A dioxane solution of the diketone was added slowly, with stirring, to an ammoniacal water solution of copper nitrate. The precipitate was filtered, washed with water, dioxane and ether, and dried. The sample was recrystallized from chloroform and sublimed at 110° at 0.005 mm. *Anal.* Calcd.: Cu, 19.87. Found: Cu, 19.25, 19.30.

4. **Bis-(2-thenoyltrifluoroacetono)-copper(II).**—An improved procedure was developed and was used in the preparation of several of the chelates.

A slurry of 11.1 g. of thenoyltrifluoroacetone (0.05 mole), 5.0 g. of copper acetate monohydrate (0.025 mole) and 100 ml. of 80% acetone–water solution was stirred for 24 hours, after which the acetone was removed on a steam-bath. The precipitate, after successive washing with ice-cold 50% water–ethanol solution, cold 5% aqueous ammonia (to remove excess copper acetate) and ice-water, was dried under vacuum and extracted in a Soxhlet extractor with 150 ml. of chloroform until the liquid extract became colorless. The chloroform solution was allowed to stand for 12 hours at room temperature and then was cooled to 0° and filtered. The dark-green crystals, superior to those produced without the extraction technique, were dried in a vacuum desiccator; yield 11.1 g. (88.7%). The compound would not sublime without decomposition. *Anal.* Calcd.: Cu, 12.56; C, 37.98; H, 1.58. Found: Cu, 12.72, 12.67; C, 38.34; H, 1.76.

5. **Bis-(2-furoyltrifluoroacetono)-copper(II).**—This compound was prepared and purified in the same manner as bis-(2-thenoyltrifluoroacetono)-copper(II). The green, crystalline compound decomposes upon sublimation; yield 99%. *Anal.* Calcd.: Cu, 13.41; C, 40.55; H, 1.69. Found: Cu, 13.87, 13.92; C, 40.07; H, 2.10.

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(18) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955).

(19) We are indebted to the Infrared Laboratory, University of Illinois, for determining in 1953 the spectra of our samples of the copper chelates of I, II, IV, V, VII, VIII, XV, XVI and XVII and of the copper chelate of acetylacetone. The other spectra were measured at the University of Nebraska Spectroscopy Laboratory.

(20) D. Wenz, M.S. Thesis, University of Nebraska, 1955.

(21) G. T. Morgan and A. E. Rawson, *J. Soc. Chem. Ind.* (*London*), **44**, 462t (1925).

6. **Bis-(2-thenoylperfluorobutyrylmethane)-copper(II).**—The method described for bis-(2-thenoyltrifluoroacetono)-copper(II) was used. The green, crystalline compound decomposes with sublimation; yield 99%. *Anal.* Calcd.: C, 33.92; H, 1.41. Found: C, 34.20; H, 1.43.

7. **Bis-(2-furoylperfluorobutyrylmethane)-copper(II).**—The compound was prepared and purified by the method described for bis-(2-thenoyltrifluoroacetono)-copper(II). The green, crystalline compound decomposes with sublimation; yield 98%. *Anal.*: Calcd. C, 35.53; H, 1.48. Found: C, 35.63; H, 1.32.

8. **Bis-(3-chloro-2,4-pentanediono)-copper(II).**—The method was similar to that described for bis-(2-thenoyltrifluoroacetono)-copper(II). A mixture of 44.6 g. of crude 3-chloro-2,4-pentanedione[22] (0.318 mole), 33.3 g. of copper acetate monohydrate (0.166 mole) and 200 ml. of acetone was allowed to stand in a stoppered flask for 24 hours. The crude precipitate, which was filtered from the slurry after cooling to 0°, was three times stirred with 200 ml. of water, filtered and dried on a fritted disc; yield 60 g. (80%). A small sample was recrystallized successively from benzene and chloroform and dried 48 hours in a vacuum desiccator. The green crystals decompose with sublimation and are unstable in alcohol and dilute, aqueous ammonia. *Anal.* Calcd.: Cu, 19.21; C, 36.31; H, 3.63. Found: Cu, 19.42; C, 35.93; H, 3.69.

9. **Bis-(3-bromo-2,4-pentanediono)-copper(II).**—A mixture of 25 g. of acetylacetone (0.25 mole) and 25 ml. of chloroform was placed in a 500-ml. three-neck, round-bottom flask fitted with a dropping funnel, stirrer and a tube leading to an aspirator (to remove hydrogen bromide). The aspirator was adjusted so that pressure inside the flask was approximately 50 mm. less than atmospheric pressure. The flask was immersed in an ice-bath and stirring commenced. A solution of 44 g. of bromine (0.275 mole) in 115 ml. of chloroform was added through the dropping funnel during a period of one-half hour, after which stirring was continued for an additional one-half hour. The solution was washed in a separatory funnel (good hood required) with eight 100-ml. portions of cold tap water. The last portion of wash water had a *p*H over 5. After removal of the chloroform under reduced pressure at room temperature, the remaining liquid was combined with 25 g. of copper(II) acetate monohydrate (0.125 mole) and 200 ml. of a 90% acetone–water mixture. After the slurry had stood for 24 hours, it was cooled to 0° and filtered. The green powder was washed by stirring three times with 200 ml. of water and dried; yield 60 g. (75%, calculated from acetylacetone). A sample was recrystallized twice from benzene and dried 48 hours in a vacuum desiccator. The compound decomposes upon sublimation and is unstable in alcohol and in dilute, aqueous ammonia. *Anal.* Calcd.: Cu, 15.14; C, 28.64; H, 2.86. Found: Cu, 15.37; C, 28.61; H, 3.04.

10. **Bis-(3-iodo-2,4-pentanediono)-copper(II).**—The chelate was precipitated by adding a water solution of copper(II) acetate monohydrate to an acetone solution of 3-iodo-2,4-pentanedione prepared by the method of Kumler.[23] Inasmuch as every attempt to recrystallize the chelate resulted in decomposition, the product never was obtained in really pure form. *Anal.* Calcd.: C, 23.37; H, 2.34. Found: C, 20.58; H, 2.17.

11. **Bis-(3-benzyl-2,4-pentanediono)-copper(II).**—A method used in previous work in this Laboratory[4] involved refluxing the sodium salt of acetylacetone with benzyl chloride, followed by fractional distillation under reduced pressure. The following new procedure represents some improvement over the former procedure. A mixture of 10 g. of sodium acetylacetonate (0.082 mole) and 14 g. of benzyl bromide (0.082 mole) was placed in a 250-ml. flask fitted with a reflux condenser. Approximately 150 ml. of nitrobenzene was added to raise the boiling temperature of the solution and for convenience in later separation of the product (soluble in nitrobenzene) from excess sodium acetylacetonate (relatively insoluble). The mixture was refluxed for eight hours and filtered. The filtrate was distilled at 90° and 10 mm. pressure until no more distillate came over. The solution obtained by dissolving the residue in 80 ml. of acetone was mixed with 10 g. of copper(II) acetate monohydrate (0.05 mole) and 20 ml. of water. After the mixture had stood for 24 hours, the precipitate was filtered off and washed four times by stirring in water and filtering. The dark grey compound, after drying, weighed 8 g. (25%). A small sample was recrystallized four times from 95% ethanol. The infrared spectrum of this sample was the same as the spectrum of a sample previously prepared by the other method and characterized by analysis.

1,3-Diketones.—Samples of 3-chloro-2,4-pentanedione, 3-ethyl-2,4-pentanedione, 3-*n*-propyl-2,4-pentanedione, 3-phenyl-2,4-pentanedione and 3-benzyl-2,4-pentanedione were prepared in our laboratories subsequent to preparing the copper chelates.[3,4] Purified samples of these diketones were recovered from the pure copper chelates by the following procedure. Approximately 1.5 g. of the copper chelate was decomposed by stirring for two hours in 100 ml. of 20% sulfuric acid, followed by washing the acid solution with three 10-ml. portions of ether. The ether washings were dried over 10 g. of anhydrous sodium sulfate for 24 hours and filtered. The sodium sulfate was washed with 10 additional ml. of dry ether and the washing added to the original ether filtrate. After removal of the ether under reduced pressure, the remaining oil was transferred to a vacuum, microdistillation apparatus and distilled. For 3-phenyl-2,4-pentanedione, which is a solid at room temperature, recrystallization from petroleum ether was used in place of the distillation step.

Samples of 1,3-diphenyl-1,3-propanedione and 1-phenyl-1,3-butanedione, purchased from Eastman Kodak Company, were recrystallized three times from 95% ethanol. Samples of 2-furoyltrifluoroacetone, 2-thenoyltrifluoroacetone, 2-furoylperfluorobutyrylmethane and 2-thenoylperfluorobutyrylmethane, purchased from the Midcontinent Chemical Company, were purified by vacuum distillation. Acetylacetone, purchased from Eastman Kodak Company, was purified by distillation.

Efforts to prepare sufficiently pure samples of 3-bromo-2,4-pentanedione and 3-iodo-2,4-pentanedione failed because of their instability. An attempt to alkylate acetylacetone by refluxing a solution of sodium acetylacetonate and methyl iodide in ethylene glycol likewise was unsuccessful.

Methods of Analysis.—Analysis for copper was made by means of a standard potassium iodide–sodium thiosulfate titration, using a starch indicator. Prior to titration, the chelates were decomposed (1) with 20% sulfuric acid, or (2) by heating followed by treatment with concentrated nitric and sulfuric acids, or (3) by precipitation with hydrogen sulfide followed by treatment of the precipitated sulfide with concentrated nitric and sulfuric acids.

Carbon–hydrogen analyses were performed by the Micro-Tech Laboratories, Skokie, Illinois.

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