presumably *via* these low lying ligand π-levels. This is indicated by the anomalous intensities of "spin-forbidden" transitions, the rather general absorption noted for some of the metals, and finally the rather large trigonal splittings. Evidence from spin-forbidden transitions of $Cr(acac)_3$ for considerably increased d_π–ligand π-interaction in the acetylacetonates over the oxalates already has been presented.[3]

In Table I we present a comparison of the crystal field parameters found in this work with earlier results. There are the usual trends of *Dq* with one striking exception—the rather low value of $Ti(acac)_3$. We can find no sensible explanation for this. The signs of the *K* values are all positive with the exception of vanadium, which shows here the same anomalous behavior as in the oxalate. Perhaps the source of this anomaly lies in the fact that we have used the approximation of neglecting off-diagonal trigonal field matrix elements. Alteration of the sign of the trigonal field parameter was not observed for metal ions in corundum.[12]

TABLE I

CRYSTAL FIELD PARAMETERS, CM.$^{-1}$

		Dq		*K*	
	$M(H_2O)_6^{3+}$	$M(C_2O_4)_3^{3-}$	$M(acac)_3$	$M(C_2O_4)_3^{3-}$	$M(acac)_3$
Ti	2030	<2400	1300–1400	>0	$+700$–1500
V	1800	1700	1800	-230	~ -900
Cr	1760	1770	1810	$+270$	$+500$
Mn	2100	1700	~ 1700	$+500$	$\sim +500$
Fe	1400	1500	~ 1640	...	...
Co	1910	~ 2000	~ 2100	-100	$+600$

Acknowledgment.—We wish to thank Mr. Mark L. Miller (University of Illinois) for remeasuring the crystal spectra of the titanium and manganese acetylacetonates. This work was supported at the University of Illinois by a grant and a coöperative fellowship (R. L. C.) from the National Science Foundation and at Brown University by a grant from the National Science Foundation and by the Materials Science Center.

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(12) D. S. McClure, *J. Chem. Phys.*, **36**, 2757 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Reaction of Metal Carbonyls with β-Diketones to Produce β-Ketoenol Complexes[1a]

BY T. G. DUNNE AND F. A. COTTON[1b]

Received September 18, 1962

It is reported that some β-ketoenol complexes of transition metals can be prepared by refluxing the metal carbonyl in the neat β-diketone. Examples reported here are $Mo(C_5H_7O_2)_3$, $Mo(C_5H_4F_3O_2)_3$, $Cr(C_5H_7O_2)_3$, $Cr(C_5H_4F_3O_2)_3$, and $Fe(C_5H_7O_2)_3$. The molybdenum compounds are the first reported β-ketoenol complexes of Mo(III) and are described in some detail. Tris-(trifluoroacetylacetonato)-chromium(III) is also a new compound and is described adequately.

Introduction

It already has been shown in several instances that metal carbonyls can be used in synthesis as, effectively, sources of reactive, zero-valent metals. Thus, to choose two examples which happen to be familiar to the authors, metal carbonyls react with the weak acid cyclopentadiene to give π-cyclopentadienyl compounds[2] and $Mo(CO)_6$ reacts with carboxylic acids to give Mo^{II} carboxylates.[3] This paper reports a study of the feasibility of the reaction of metal carbonyls with β-diketones as a preparative method for metal β-ketoenolates. The genesis of this study was the observation by Dr. F. Calderazzo, in this Laboratory, that $Mo(CO)_6$ reacts with refluxing 2,4-pentanedione to give a brown, air-sensitive, crystalline substance which shows no infrared absorption in the range (2200–1700 cm.$^{-1}$) characteristic of the Mo–CO group. The present authors have shown that Calderazzo's compound is Mo^{III} acetylacetonate, a hitherto unknown substance, and subsequently have investigated the reactions of other metal carbonyls with acetylacetone and other β-diketones. This work has resulted in the preparation and characterization of several new compounds as well as the discovery of new methods for preparing some previously known compounds. In this paper we describe several reactions which are quite straightforward. Further studies of the scope and mechanism of the reaction have been made and are continuing; these will be the subject of a later report. We also describe here the characterization of two Mo(III) tris-β-ketoenol complexes which are the first such compounds of Mo(III) to be characterized and a new β-diketone complex of Cr(III).

Results and Discussion

In this paper we report the preparation of the five compounds: $Mo(C_5H_7O_2)_3$, $Mo(C_5H_4F_3O_2)_3$, $Cr(C_5H_7O_2)_3$, $Cr(C_5H_4F_3O_2)_3$, and $Fe(C_5H_7O_2)_3$, where $C_5H_7O_2^-$ is the enol anion of pentane-2,4-dione and $C_5H_4F_3O_2^-$ is the enol anion of 1,1,1-trifluoropentane-2,4-dione. All of these compounds can be prepared rather easily and in good yield by refluxing a mixture of the appropriate mononuclear

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(1) (a) Supported by the National Science Foundation; (b) Fellow of the Alfred P. Sloan Foundation.

(2) G. Wilkinson, *J. Am. Chem. Soc.*, **76**, 209 (1954).

(3) E. Bannister and G. Wilkinson, *Chem. Ind.* (London), 319 (1962).

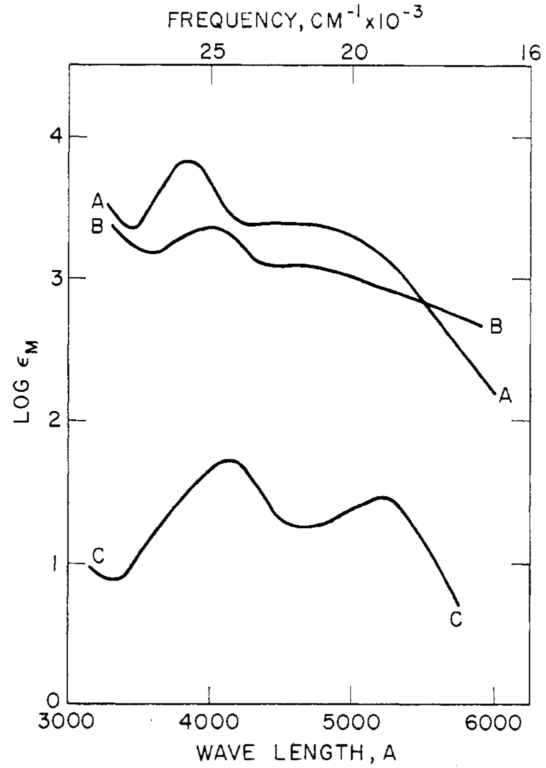

Fig. 1.—Visible and near ultraviolet spectra of Mo(III) complexes: A, $Mo(C_5H_7O_2)_3$; B, $Mo(C_5H_4F_3O_2)_3$; C, $[MoCl_6]^{3-}$, from ref. 6.

metal carbonyl with the neat β-diketone. The stoichiometry of the reactions is apparently that given in eq. 1, according to the volumes of gas evolved, but a firm

$$M(CO)_n + 3HL \longrightarrow ML_3 + {}^3/_2H_2 + nCO \qquad (1)$$

conclusion about this must await the completion of mass spectrometric studies of the gaseous reaction products.

In all cases so far studied, $Mo(CO)_6$ reacts considerably faster than $Cr(CO)_6$. With some β-diketones other than those considered here, compounds with metals in valence states other than (III) are obtained; these reactions will be described later.

The compounds $Cr(C_5H_7O_2)_3$ and $Fe(C_5H_7O_2)_3$ are, of course, well known and obtainable by other reactions which probably are more convenient.[4] They were prepared here just because they are well characterized and thus the identity of the products of our reaction with these compounds as prepared by different routes tends to confirm our formulation of the products in other cases.[4a] The three compounds $Mo(C_5H_7O_2)_3$, $Mo(C_5H_4F_3O_2)_3$, and $Cr(C_5H_4F_3O_2)_3$ which have not, to our knowledge, been described previously in the literature, will now be discussed.

$Mo(C_5H_7O_2)_3$.—The only prior reference[4a] to the existence of this molecule is the report by Jarrett[5] that crystals of $Al(C_5H_7O_2)_3$ containing *ca.* 1% of $Mo(C_5H_7O_2)_3$ were studied by electron spin resonance. No indication was given as to whether pure $Mo(C_5H_7O_2)_3$ had been isolated, as to how the crystals of the compound in $Al(C_5H_7O_2)_3$ were prepared, or whether any criteria aside from the e.s.r. results themselves had been used to show that $Mo(C_5H_7O_2)_3$ molecules were present. It therefore seems reasonable to describe $Mo(C_5H_7O_2)_3$ as a new compound. The e.s.r. results reported by Jarrett were consistent with the presence of a species having a spin quartet ground state with $g_\perp = 1.94$ and $g_\parallel = 3.94$ (the reference axis being the principal axis, C_3, of the molecule having D_3 symmetry). A rather large zero field splitting also was postulated to explain the observed e.s.r. spectrum.

The pure compound, $Mo(C_5H_7O_2)_3$, has the following properties. It is a dark, red-brown solid which can be sublimed under high vacuum below its melting point, 229–231°. It is rapidly and exothermically attacked by oxygen, though this is not particularly noticeable visually in its early stages. It is soluble in acetone, aromatic hydrocarbons, and carbon tetrachloride (with which it slowly reacts) to give red-brown solutions, but is relatively insoluble in aliphatic hydrocarbons. It has an effective magnetic moment at room temperature of 3.8 ± 0.1 B.M., which is in accord with the theoretical expectation for an essentially octahedrally coördinated d^3 ion having a spin-orbit coupling constant of 200–300 $cm.^{-1}$, and checks with the g values reported by Jarrett.[5]

Jarrett has reported that $Mo(C_5H_7O_2)_3$ is monoclinic with the a and b cell edges nearly identical with those of $Al(C_5H_7O_2)_3$. Comparison of the X-ray powder patterns of the two substances has shown, however, that they are not isomorphous. The data for $Mo(C_5H_7O_2)_3$ are given in the Experimental section. It was considered that the greater size of the metal atom in $Mo(C_5H_7O_2)_3$ might have been chiefly responsible for the difference in structure and that this compound therefore might be isomorphous with $In(C_5H_7O_2)_3$ or $Ga(C_5H_7O_2)_3$. However, the latter is isomorphous with $Al(C_5H_7O_2)_3$, and the former is not isomorphous with $Mo(C_5H_7O_2)_3$ or with $Al(C_5H_7O_2)_3$.

The infrared spectrum of $Mo(C_5H_7O_2)_3$ (Table II) is entirely in accord with the proposed tris-chelate structure, as may be seen by comparison with the data for the chromium and iron compounds.

The visible spectrum of $Mo(C_5H_7O_2)_3$ in acetone is shown along with that of $Mo(C_5H_4F_3O_2)_3$ in the same solvent in Fig. 1. Also shown for comparison is a portion of the spectrum of $[MoCl_6]^{3-}$ as reported by Hartmann and Schmidt.[6] It will be seen that the spectra are qualitatively similar but those of the β-ketoenol complexes differ quantitatively from that of $[MoCl_6]^{3-}$ in two respects. First, the bands occur at higher energies. This is to be expected because the β-ketoenol oxygen atoms lie further to the strong end of the spectrochemical series (close to H_2O) than the Cl^- ion, and the bands have been attributed to d–d transitions, *viz.*, the ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions of the

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[4] See W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 105 (1957).

[4a] Note Added in Proof.—M. L. Larson and F. W. Moore, *Inorg. Chem.*, **1**, 856 (1962), recently have reported the preparation of $Mo(C_5H_7O_2)_3$ by the method we have used and also by an independent and more conventional method which tends to substantiate the structure proposed.

[5] H. S. Jarrett, *J. Chem. Phys.*, **27**, 1298 (1957).

[6] H. Hartmann and H.-J. Schmidt, *Z. physik. Chem.* (Frankfurt), **11**, 234 (1957).

octahedral d^3 system.[7] Second, the transitions are about ten times more intense in the β-ketoenol complexes than in $[MoCl_6]^{3-}$. This presumably is attributable to greater charge transfer character, but in the absence of further data cannot be discussed more explicitly. It also may be noted that fluorine substitution causes the spectrum in the β-ketoenol complexes to move slightly to lower energies. This is as expected, the fluorine substitution making the ligand less basic, and an analogous effect has been observed with Cu(II) β-ketoenol complexes.[8]

The positions of the bands, in cm.$^{-1}$, and the decadic molar extinction coefficients, in parentheses, are: $Mo(C_5H_7O_2)_3$: 27,000 (5 × 10^3), ~23,300 (sh); $Mo(C_5H_4F_3O_2)_3$: 24,400 (2 × 10^3), ~22,200 (sh).

$Mo(C_5H_4F_3O_2)_3$.—This is a dark brown-black solid which sublimes fairly easily under vacuum and has a melting point (sealed tube, 1 atm. N_2) of 155–157°. It also is sensitive to oxygen, probably even more so than is the acetylacetonate. It is soluble in benzene and acetone but insoluble in aliphatic hydrocarbons. It has an effective magnetic moment of 3.8 ± 0.1 B.M. at room temperature. Its visible spectrum has been discussed above. Its infrared spectrum, summarized in Table II, is consistent with the assumed structure and quite similar to that of its chromium analog.

$Cr(C_5H_4F_3O_2)_3$.—A molecule of this formula has been mentioned by Jarrett[5] as existing in crystals of the analogous aluminum complex but the pure compound does not appear to have been described previously. The compound is a gray-green crystalline solid, which sublimes under vacuum and has a melting point (sealed tube, 1 atm. N_2) of 124–126°. It is soluble in acetone and benzene but insoluble in aliphatic hydrocarbons. Its infrared spectrum is summarized in Table II. It has an absorption band in the visible at 17,700 cm.$^{-1}$, that is, at slightly lower energy than that for chromium(III) acetylacetonate (17,900 cm.$^{-1}$).

Experimental

Preparation of Compounds. $Mo(C_5H_7O_2)_3$.—$Mo(CO)_6$ (10 g.) and acetylacetone (40 ml.) were added to a 100-ml. 3-neck flask flushed with prepurified nitrogen. The flask then was evacuated and flushed with nitrogen several times. The mixture was held at reflux (~135°) for 2 days under a slight positive pressure of nitrogen. After cooling, the excess acetylacetone was removed by vacuum evaporation leaving a brown solid and a small amount of unreacted $Mo(CO)_6$; 30 ml. of nitrogen-saturated benzene was added, the solution was filtered, and 100 ml. of nitrogen-saturated *n*-heptane was added, which precipitated a nicely crystallized red-brown solid. This was separated by filtration and vacuum dried; yield, 6 g.

Anal. Calcd. for $Mo(C_5H_7O_2)_3$: C, 45.81; H, 5.38; Mo, 24.40. Found: C, 45.7; H, 5.68; Mo, 23.8. The compound is quite air-sensitive and must be handled under an inert atmosphere at all times.

$Mo(C_5H_4F_3O_2)_3$.—In the same manner as above, $Mo(CO)_6$ (5 g.) and trifluoroacetylacetone (25 ml.) were allowed to react at reflux (~107°) for 4 days. After removal of excess trifluoroacetylacetone, crystallization was carried out by addition of 100 ml. of *n*-heptane to 18 ml. of a benzene solution. The well crystallized brown product was vacuum dried; yield, 1 g.

Anal. Calcd. for $Mo(C_5H_4F_3O_2)_3$: C, 32.45; H, 2.18. Found: C, 32.6; H, 2.46. This compound is also air-sensitive.

$Cr(C_5H_7O_2)_3$.—$Cr(CO)_6$ (6 g.) and acetylacetone (40 ml.) were allowed to react under prepurified nitrogen for 16 hr. at 135°. The reaction mixture was initially a brilliant green, but soon became red-violet. Excess acetylacetone was removed and the product was recrystallized in air by dissolving it in 20 ml. of benzene, filtering, and precipitating large red-violet crystals by the addition of 30 ml. of petroleum ether; yield, 3 g.

Anal. Calcd. for $Cr(C_5H_7O_2)_3$: C, 51.58; H, 6.05. Found: C, 51.7; H, 5.87.

$Cr(C_5H_4F_3O_2)_3$.—$Cr(CO)_6$ (5 g.) and trifluoroacetylacetone (28 ml.) were heated under nitrogen for 2 days at 104°. Excess trifluoroacetylacetone was removed and the product was recrystallized by dissolving it in 20 ml. of benzene, filtering, and precipitating as a black crystalline solid; yield, 2 g.

Anal. Calcd. for $Cr(C_5H_4F_3O_2)_3$: C, 35.24; H, 2.31. Found: C, 35.5; H, 2.78.

$Fe(C_5H_7O_2)_3$.—Acetylacetone (30 g.) and $Fe(CO)_5$ (6.5 g.) were allowed to react under nitrogen for 30 hr. at 135° in a 200-ml. 3-neck flask, shielded from light. Excess acetylacetone was removed and the solid recrystallized from acetone solution by addition of water; the resulting precipitate was recrystallized a second time by adding *n*-heptane to a benzene solution. A well crystallized red product resulted; yield, 1 g.

Anal. Calcd. for $Fe(C_5H_7O_2)_3$: C, 50.99; H, 6.00. Found: C, 51.3; H, 6.11.

$Al(C_5H_7O_2)_3$.—This was prepared by the method of *Inorganic Syntheses*, **2**, 25 (1946).

$Ga(C_5H_7O_2)_3$.—$Ga(NO_3)_3 \cdot 12H_2O$ (0.220 g.) was dissolved in H_2O and 2 ml. of 1 *M* $NH_4C_5H_7O_2$ was added. A white solid precipitated which was dissolved in benzene and recrystallized by adding *n*-heptane.

Anal. Calcd. for $Ga(C_5H_7O_2)_3$: C, 49.09; H, 5.77. Found: C, 49.4; H, 5.91.

Visible and Ultraviolet Spectra.—In order to minimize reaction of the Mo(III) complexes with oxygen, samples were weighed out under prepurified nitrogen and solvent was distilled directly onto the sample in a nitrogen-flushed apparatus. All dilutions were made with solvent freshly distilled under nitrogen and spectra were run immediately. Even so, decomposition took place during the determination of the spectra. The decomposition resulted in a decrease in intensity of observed bands at a rate such that the reported extinction coefficients could be low by perhaps 20% for both $Mo(C_5H_7O_2)_3$ and $Mo(C_5H_4F_3O_2)_3$. The effect of decomposition in the ultraviolet region was somewhat more evident, perhaps because of the smaller concentrations used. Decomposition had essentially no effect on band positions. Measurements were made using Cary spectrophotometers, Models 14 and 11.

Magnetic Measurements.—Room temperature magnetic moments were measured by the Gouy method using $CoHg(CNS)_4$ as a calibrant. The magnetic moments of $Cr(C_5H_7O_2)_3$ and $Fe(C_5H_7O_2)_3$ were checked by the *t*-butyl alcohol proton resonance shift on adding the complex to benzene containing 2% *t*-butyl alcohol.[9] In this method it is essential to use an accurately concentric double-walled sample tube (Wilmad Glass Company, Buena, N. J.) containing the solvent in the outer tube and sample in the inner tube. On the Varian Associates A-60 spectrometer this method allows a rapid and reasonably good check on μ_{eff}, although the accuracy is somewhat less than that of the Gouy method. For $Cr(C_5H_7O_2)_3$ a solution containing 2.61 × 10^{-2} g./ml. gave a fractional frequency shift, $\Delta f/f$, of 9.1 × 10^{-7}, and for $Fe(C_5H_7O_2)_3$ a solution containing 1.02 × 10^{-2} g./ml. gave a fractional shift of 8.2 × 10^{-7}. In all cases, diamagnetic

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(7) *Cf.* T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 292.

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

(9) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

TABLE I

MAGNETIC MOMENTS OF THE COMPLEXES

Compound	Temp., °K.	μ_{eff}, B.M. Found	μ_{eff}, B.M. Lit.
$Mo(C_5H_7O_2)_3$	302	3.82	3.80[a]
$Mo(C_5H_4F_3O_2)_3$	302	3.76	...
$Cr(C_5H_7O_2)_3$	299	3.7 ± 0.15[b]	3.86[c]
$Fe(C_5H_7O_2)_3$	299	5.7 ± 0.15[b]	5.95[d]

[a] Computed from the *g* values for $Mo(C_5H_7O_2)_3$ in $Al(C_5H_7O_2)_3$ reported by Jarrett.[5] [b] Obtained from proton magnetic resonance shifts of solutions; see Experimental section. [c] From ref. 5. [d] From L. Cambi and S. Szego, *Ber.*, **64**, 2591 (1931).

corrections were made using Pascal's constants.[10] The results are recorded in Table I.

X-Ray Powder Patterns.—These were recorded with standard equipment using MoKα radiation for $In(C_5H_7O_2)_3$ and CuKα radiation for the other compounds. For $Mo(C_5H_7O_2)_3$, the following *d* values, in Å., and relative intensities of lines were found: 8.34 m, 7.90 m, 7.50 s, 2.98 vw, 6.61 ms, 6.07 ms, 5.27 m, 4.11 mw, 3.85 w, 3.78 ms, 3.52 vw, 3.25 w, 2.92 w, 2.85 w, 2.70 w, 2.61 vw, 2.49 vw, 2.37 vw, 2.30 vw, 2.10 vvw, 2.03 vvw (v, very; w, weak; m, medium; s, strong).

TABLE II

PRINCIPAL INFRARED ABSORPTION BANDS (CM.$^{-1}$) OF THE COMPLEXES OBSERVED IN CCl_4 SOLUTION

$Fe(C_5H_7O_2)_3$[a]	Cr-$(C_5H_7O_2)_3$[b]	Mo-$(C_5H_7O_2)_3$	Cr-$(C_5H_4F_3O_2)_3$	Mo-$(C_5H_4F_3O_2)_2$
1572	1578	1563	1603	1582
1526	1523	1521	1530	1522
1425	1435	1431	1445	1432
1390 (1365 sh)	1390	1378	1364	1366
1276	1280	1273	1303	1302
1190	1195	1195	1226	1230
1022	1025	1022	1203	1204
930	932	932	1158	1159
663	682	673	1141	1140
654	662	655	...	...
			1017	1015
			953	947
			867	868

[a] Data from K. Nakamoto, *et al.*, *J. Am. Chem. Soc.*, **83**, 1066 (1961), where assignments are proposed. [b] These data are in good agreement with those of Nakamoto (footnote *a*) for Cr-$(C_5H_7O_2)_3$.

Infrared Spectra.—These were measured on a Perkin-Elmer Model 21 spectrophotometer equipped with a rock-salt prism. Solutions of the molybdenum compounds were prepared and loaded into nitrogen-flushed cells in a nitrogen atmosphere.

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[10] P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1956, pp. 91-95.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA,
AND CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO

The Reaction of Pyridine with Cobalt(II) Acetylacetonate in Benzene. Evidence for a Polymeric Species[1]

BY JOHN P. FACKLER, JR.

Received October 24, 1962

The reaction of pyridine with anhydrous cobalt(II) acetylacetonate has been studied spectrophotometrically in oxygen-free benzene. Evidence is presented for species containing cobalt to pyridine ratios of 2:1, 1:1, and 1:2. The species $[Co(AA)_2]_2py$ has been isolated from the system. Equilibrium constants for the formation of $Co(AA)_2py$ and $Co(AA)_2(py)_2$ have been determined. Visible spectra for these species as well as $[Co(AA)_2]_2py$ and $Co(AA)_2$ are presented and discussed.

Introduction

In a series of papers,[2] the intermolecular association of nickel(II) acetylacetonate in hydrocarbon solutions was definitely established. The premise that an oxygen on chelating ligands may act to bridge two $Ni(AA)_2$ units was given additional support by the isolation[2] of $[Ni(AA)_2]_2py$ from the reaction of pyridine with anhydrous $[Ni(AA)_2]_3$ in benzene. It is becoming apparent that intermolecular association of this type has given rise to many of the so-called "anomalous" magnetic and spectral properties of neutral chelate complexes of nickel(II).[3] The spectrophotometric titration of $Ni(AA)_2$ with pyridine in benzene[2] suggested the absence of any stable 1:1 adducts of pyridine with $Ni(AA)_2$, unlike the reaction[4] of pyridine with $Cu(AA)_2$.

The possibility that intermolecular association may generally occur with β-diketonate complexes of bivalent transition metals is currently being examined in view of the recent work with nickel. Cotton and Holm[5] suggested that spin-free (μ_{eff} = 4.8-5.0 B.M.) complexes of cobalt(II) with singly charged anionic ligands of the acetylacetonate type may be planar. The structural arguments based on spectral and magnetic properties alone have since been shown to be subject to question by the isolation and structural determination of tetrahedral cobalt(II) dipivaloylmethide.[6] Moreover, it was shown recently that some

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[1] This work was presented, in part, at the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J. Inquiries should be directed to the author at Case Institute of Technology.

[2] J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962), and references therein.

[3] R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **1**, 599 (1962), and references therein; but see also R. H. Holm and K. Swaminathan, *ibid.*, **2**, 181 (1963).

[4] D. P. Graddon, *Nature*, **183**, 1610 (1959); W. R. Walker, *Australian J. Chem.*, **14**, 161 (1961).

[5] F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **82**, 2979 (1960).

[6] F. A. Cotton and R. H. Soderberg, *ibid.*, **84**, 873 (1962).