cyclic, benzyl, and picolyl did not. Derivatives of five- or higher-membered cyclic amines can be classed with the *n*-alkyl derivatives.

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β-Diketone Complexes of Cobalt(III). III. Tris(β-diketonato)cobalt(III) and Bis(acetylacetonato)diaminecobalt(III) Trichelate Species[1a]

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The two geometrical isomers of tris(2,2-dimethyl-3,5-hexanedionato)cobalt(III) have been prepared, separated chromatographically, and identified by proton magnetic resonance (pmr) spectroscopy. The pmr of a series of bis(acetylacetonato)diaminecobalt(III) complexes (diamine = ethylenediamine, N,N,N′,N′-tetramethylethylenediamine, 2,2′-bipyridine, or 1,10-phenanthroline) show the importance of both diamagnetic ring anisotropy and external environmental effects. Marked improvements have been made in the synthesis of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III) and tris(1,1,1,5,5,5-hexafluoroacetylacetonato)cobalt(III). Electronic and vibrational energy levels are also discussed.

Introduction

A detailed study of bis(β-diketonato)cobalt(III) complexes is in progress in this laboratory to determine the σ and π ligand field effects on the reaction rates and the reaction stereochemistry of cobalt(III) complexes. Previous reports[1a,2,3] have demonstrated the usefulness of sodium dinitrobis(acetylacetonato)cobaltate(III) for the synthesis of bis(acetylacetonato)cobalt(III) complexes. A series of diamine complexes have been used to study effects on the β-diketone methyl group pmr (proton magnetic resonance) signals. The tris complexes of dhd and thd[4] have been prepared for the purpose of spectral correlations in the study of the bis complexes of these ligands now in progress. $Co(thd)_3$ has been prepared by an alternate method,[5] but no characterization has been reported. We have increased the yield of the tris complex and spectrally characterized it.

The volatility of hexafluoroacetylacetonate complexes makes them particularly useful in chemical research such as gas chromatography[6] and mass spectroscopy.[7] Unfortunately, previously reported methods of preparing the cobalt(III) complex[8,9] are less than satisfactory in terms of either yield (1%)[8] or safety (90% H_2O_2).[9] We have achieved the synthesis of $Co(hfa)_3$ in high yield with safe, commercially available reactants and are currently studying the reaction mechanism.

Results

Syntheses.—As previously reported[2,3] treatment of $Co(\beta\text{-dik})_2(NO_2)_2^-$ with amines in the presence of activated carbon results in the formation of the diamine derivatives. This procedure has been used to form the N,N,N′,N′-tetramethylethylenediamine and 1,10-phenanthroline derivatives of bis(acetylacetonato)diaminecobalt(III) perchlorate. The use of Norit A for the synthesis of the heterochelates is important. To illustrate, the reaction of *trans*-$Co(acac)_2(NO_2)_2^-$ and ammonia with neutral Norit or Norit FQP produces $Co(acac)_3$ rather than the *cis*- and *trans*-$Co(acac)_2(NH_3)_2^+$ species.[10]

The tris complexes of cobalt(III) with 2,2-dimethylhexane-3,5-dione and 2,2,6,6-tetramethylheptane-3,5-dione have been prepared in high yield by allowing

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[1] (a) Part II: B. P. Cotsoradis and R. D. Archer, *Inorg. Chem.*, **6**, 800 (1967); presented in part at 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968; (b) Department of Chemistry, University of Massachusetts, Amherst, Mass. 01002; (c) Department of Chemistry, Tulane University, New Orleans, La. 70118; (d) to whom correspondence should be sent.

[2] R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1584 (1965).

[3] L. J. Boucher, *ibid.*, **6**, 2162 (1967).

[4] Abbreviations used in this paper include: dhd, 2,2-dimethylhexane-3,5-dionato; thd, 2,2,6,6-tetramethylheptane-3,5-dionato; en, ethylenediamine; bipy, 2,2′-bipyridine; *c*-phen, 1,10-phenanthroline; acac, 2,4-pentanedionato; hfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato; tmed, N,N,N′,N′-tetramethylethylenediamine.

[5] G. S. Hammond, D. C. Nonhebel, and C. H. S. Wu, *Inorg. Chem.*, **2**, 73 (1963).

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[10] S. Golinger, unpublished results.

sodium hexanitrocobaltate(III) to react with basic solutions of the diketones. In order to attain sufficient solubility for the synthesis of the Co(thd)$_3$ complex, a mixed solvent of ethanol and water was found necessary.

The tris complex of hexafluoroacetylacetone, previously prepared in low yield by alternate methods,[8,9] has been successfully synthesized by the reaction of CoF_3 and the anhydrous ligand. In the presence of dry powdered sodium fluoride, the reaction rate is markedly increased and the yield is improved. Little, if any, of the cobalt(II) β-diketone complex is formed when water is rigorously excluded from the reaction. However, a great deal of the reduced product is formed in the presence of incompletely dehydrated reagents.

Nuclear Magnetic Resonance Spectra.—The pmr and ^{19}F magnetic resonance spectra of the new compounds are listed in Tables I and II along with more detailed chemical shift data for the previously reported[2] [Co(acac)$_2$en]ClO$_4$ and [Co(acac)$_2$bipy]I complexes. Improved instrumentation and solvent changes have resulted in the observation of a slight splitting in the diketone methyl protons (Figure 1) of the [Co(acac)$_2$en]ClO$_4$ complex which had previously been reported to show only a single methyl resonance.[2] The pmr spectra of the chromatographed isomers of Co(dhd)$_3$ (Figure 2) allow the assignment of *fac* and *mer* structures.[11,12]

Infrared Spectra.—The vibrational spectra of the compounds have been recorded in the region from 4000 to 300 cm^{-1}. Tables III and IV list the characteristic bands of the new compounds. Our spectra for the other species are in agreement with those reported previously, specifically, [Co(acac)$_2$en]ClO$_4$,[2] [Co(acac)$_2$bipy]I,[2] [Co(hfa)$_3$],[8] and Hdhd.[13]

Assignments for the coordinated acetylacetonate ligand vibrations have been made with reference to the revised assignments of the vibrational bands in tris(acetylacetonato)chromium(III) using ^{18}O labeling.[14] This places the C=O and C=C vibrations back to the order recommended by Dismukes, Jones, and Bailar.[15] Our previous assignments,[1,2] which were based on Nakamoto's normal-coordinate analysis,[16] should be revised to agree with Tables III and IV. Assignments of the *o*-phenanthroline vibrational modes has been made with reference to the work of Schilt and Taylor.[17] See also ref 18–20 for data pertinent to Table III.

Table I

Proton Chemical Shifts for Bis(acetylacetonato)cobalt(III) Complexes[a]

Complex	Solvent	CH_3 proton peak positions	Δ[b]	CH proton peak positions
[Co(acac)$_2$en]ClO$_4$[c]	CH_3OD	−2.11 −2.13	0.018[d]	−5.64
	CD_3OD	−2.13 −2.14	0.022[d]	−5.64
	$(CD_3)_2SO$	−2.08	0.018[d]	−5.61
	D_2O[e]	−2.16	0.008[d,f]	−5.77
	D_2O[g]	*h,i*	0.010	*i*
[Co(acac)$_2$tmed]ClO$_4$[j]	$CDCl_3$	−2.09 −2.20	0.11	−5.59
	CD_3OD	−2.12 −2.24	0.12	−5.76
[Co(acac)$_2$bipy]I	CD_3OD	−1.91 −2.42	0.51	−5.83
	$CDCl_3$	−1.93 −2.40	0.47	−5.32
	CH_2Cl_2	−1.91 −2.40	0.49	*k*
[Co(acac)$_2$-*o*-phen]ClO$_4$	CH_2Cl_2[l]	−1.86 −2.45	0.59	*k*

[a] Chemical shifts, ppm, relative to tetramethylsilane, 500-cps sweep width, saturated solutions, unless otherwise noted. [b] Methyl splitting. [c] Ethylenediamine CH_2 protons observed at −2.7 ppm when not obscured by solvent. [d] Splitting measured at 50-cps sweep width. [e] Chemical shifts relative to the methyl groups of sodium 3-trimethylsilyl-1-propanesulfonate. [f] Splitting obtained by Varian Associates on a precisely tuned Varian A-60 spectrometer. [g] Spectrum obtained on a Varian Model HA-100 spectrometer by Varian Associates. [h] Doublet observed. [i] No reference available. [j] N-Methyl peaks of the diamine observed at −1.81 and −2.25 ppm; latter overlaps diketonate methyl signal. [k] Peak obscured by solvent. [l] Methylene chloride is the only solvent which dissolves enough complex to obtain a pmr spectrum.

Table II

Proton Chemical Shifts[a]

Compound	*t*-Butyl proton peak positions	Methyl proton peak positions	CH proton peak positions
Hdhd	−1.15 (9)	−2.00 (3)	−5.60 (1)
	−1.15 (9)[b]	−2.05 (3)[b]	−5.60 (1)[b]
fac-Co(dhd)$_3$	−1.10 (9)	−2.16 (3)	−5.49 (1)
mer-Co(dhd)$_3$	−1.08 −1.10 (9)[c]	−2.08 −2.15 (3) −2.18	−5.41 −5.50 (1) −5.53
Co(thd)$_3$	−1.09 (18)	. . .	−5.62 (1)
Co(hfa)$_3$	. . .	. . .	−6.55[d]
	. . .	. . .	−6.95[e]

[a] Chemical shifts, ppm, relative to tetramethylsilane, CCl_4 solutions, 500 cps, integrated intensities in parentheses. [b] Neat ligand, enol proton peak at −15.77 ppm, intensity 1. [c] *t*-Butyl proton splitting observed at 50-cps sweep width. [d] $CDCl_3$ solution. [e] Acetone solution; Wojcicki and coworkers[8] erroneously reported τ 4.05 (−5.95 ppm) in CD_3COCD_3; the corresponding rhodium(III) complex in acetone, −6.93 ppm: S. C. Chattoraj and R. E. Sievers, *Inorg. Chem.*, **6**, 408 (1967). A single ^{19}F resonance was also observed at 73.3 ppm relative to $CFCl_3$.

Absorption Spectra.—The absorption peaks in the visible and ultraviolet spectral regions for the complexes are listed in Tables V and VI.

The spectral assignments have been made on the

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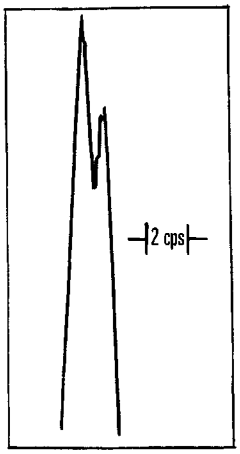

Figure 1.—Methyl splitting of $[Co(acac)_2en]ClO_4$ in D_2O at a 50-cps sweep width on a 100-Mc instrument.

basis of previous interpretations.[1,2,19,21,22] The visible peak assignments have been made on the basis of O_h microsymmetry rather than the actual symmetry of each complex.

Initially we recorded a spectrum of $Co(hfa)_3$ in CH_2Cl_2 which was in agreement with that previously published[8] showing peaks at 16,500 and 32,800 cm^{-1} and a shoulder at 29,000 cm^{-1} with no peaks observed above 32,800 cm^{-1}. The corresponding spectra of $Co(acac)_3$, *fac*- and *mer*-$Co(dhd)_3$, and $Co(thd)_3$ showed at least two more higher energy peaks. This discrepancy prompted us to obtain the spectrum of $Co(hfa)_3$ in a number of other solvents. The recorded values (Table VI) are for a cyclohexane solution of the tris complex, and the spectra are virtually identical when run in dry tetrahydrofuran or a freshly prepared solution of dry CH_2Cl_2. When run in ordinary, reagent grade CH_2Cl_2, or after standing for some time, the spectra obtained showed no higher energy peaks than 32,800 cm^{-1}. In fact, we followed the decrease in intensity of the higher energy peaks and corresponding intensity increase of the peak at 32,800 cm^{-1} in a stoppered solution of dry CH_2Cl_2. Attempts to run the spectrum of $Co(hfa)_3$ in CH_3OH resulted in decomposition to the orange color of the Co(II) species. The ultraviolet spectrum of the decomposed species is similar to that obtained in ordinary CH_2Cl_2.

Discussion

Synthesis.—Kilner, Hartman, and Wojcicki[8] have obtained $Co(hfa)_3$ in only about 1% yield from the reaction of $Co_2(CO)_8$ and the neat ligand. The only other previously reported method[9] requires the use of 90% hydrogen peroxide (a safety hazard). While a good yield was obtained for the reaction of CoF_3 and the neat ligand in our laboratory, the addition of sodium fluoride allowed an increase in the reaction rate and the product yield. Fluoride ion is able, as a Brønsted base, to remove protons and/or HF from the reaction mixture. Since CoF_3 is a polymer,[23] the fluoride ion may also help break down the solid lattice. A very important aspect of the reaction appears to be the necessity of rigorous exclusion of water from the

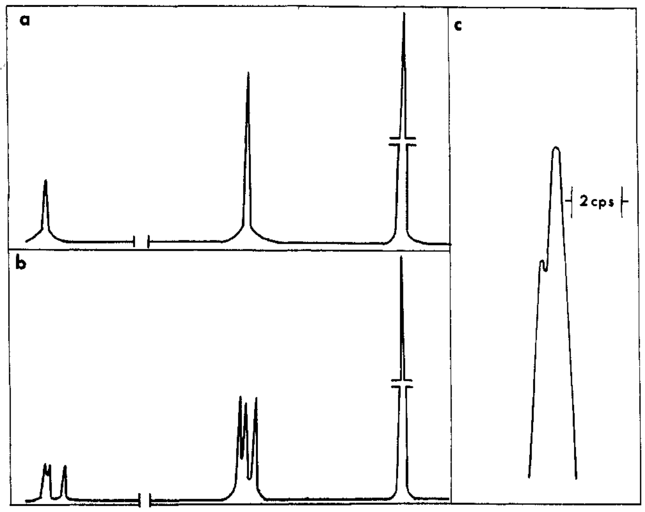

Figure 2.—(a) *fac*-$Co(dhd)_3$ proton resonance spectrum in CCl_4 *vs.* TMS; (b) *mer*-$Co(dhd)_3$ proton resonance spectrum in CCl_4 *vs.* TMS at a 500-cps sweep width; (c) *mer*-$Co(dhd)_3$ *t*-butyl signal at a 50-cps sweep width.

TABLE III

CHARACTERISTIC INFRARED SPECTRAL PEAKS OF $[Co(acac)_2L_2]ClO_4$ COMPLEXES[a]

tmed	*o*-phen	Assignment
3010 w–m	3100 w–m	C–H str
2940 w–m	2980 w–m	C–H str
1563 s	1565 s	C$\overset{\cdots}{-}$O str[b]
1520 s	1518 s	C$\overset{\cdots}{-}$C str[b]
	1462 m	py ring vib
1427 m	1430 s	CH_3 asym bend
1363 s	1361 s	CH_3 sym bend
1284 m	1286 s	acac[c]
1090 s	1102 s 1078 s	ClO_4^- vib
1034 m	1028 m	CH_3 rock
950 m	950 m	acac[c]
	942 m	
	845 s	Ring H (py) out-of-plane bend
800 s	805 m	Ring H (acac) out-of-plane bend
760 m	788 s	
690 w–m	693 w	Ring def and M–O str
657 m	661 m	Out-of-plane def
615 s	625 m–s	ClO_4^- vib
535 w		
505 w	520 w	M–O str
475 m	478 m	Combination band and/or M–N str
435 vw	440 w	In-plane O–M–O bend

[a] Spectral intensities: s, strong; m, medium; w, weak; b, broad; vw, very weak; readings in cm^{-1}. [b] Earlier papers in this series had these bands reversed based on ref 16 and 18, but recent work by Pinchas and coworkers[14] substantiates the position of Boucher and Bailar and coworkers[15,19,20] that the higher frequency band is primarily a C=O stretch. [c] See ref 16.

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TABLE IV

CHARACTERISTIC INFRARED SPECTRAL PEAKS OF TRIS-β-DIKETONE COMPLEXES[a]

fac-Co(dhd)$_3$[b]	*mer*-Co(dhd)$_3$[b]	Co(thd)$_3$[c]	Assignments
2980 m	2970 m	2960 s	C-H str
1574 s	1580 s	1575 s	C $\overset{\cdots}{—}$ O str
		1561 s	
1508 s	1514 s	1525 s	C $\overset{\cdots}{—}$ C str
		1496 s	
1389s	1391 m	1398 s	*t*-Butyl C–H bend
1361 m	1366 w	1382 s	*t*-Butyl C–H bend
		1357 s	
1284 w	1289 w		
1164 w		1178 s	
		1149 s	
1020 w	1015 w	1020 s	CH_3 rock
		962 w	
734 s	747 s	749 s	Ring H (dik) out-of-plane bend
	695 w		
660 w	675 w	655 s	Out-of-plane def
510 w	510 w	518 m	M–O str
		453 w	In-plane O–M–O bend

[a] Spectral intensities: s, strong; m, medium; w, weak; readings in cm^{-1}. [b] CCl_4 solutions between AgCl windows. [c] KBr pellet.

TABLE V

VISIBLE AND ULTRAVIOLET SPECTRA OF $[Co(acac)_2L_2]ClO_4$ COMPLEXES[a]

Assignments	tmed	*o*-phn
$^1A_{1g} \rightarrow {}^1T_{1g}$	16,600 (2.11)	17,700 (2.09)
$^1A_{1g} \rightarrow {}^1T_{2g}$		24,600 sh
$t_{2g} \rightarrow \pi^*$	30,200 sh[b]	29,800 sh
$\pi \rightarrow \pi^*$	33,800 sh	33,800 sh
$\pi \rightarrow \pi^*$	38,400 (4.43)	37,600 (4.55)
$\pi \rightarrow \pi^*$	42,200 (4.51)	43,900 (4.80)

[a] The methanol solution peaks are given in cm^{-1} with the molar extinction coefficient logarithmic values (log ε) indicated in parentheses. [b] Shoulder; cm^{-1} values only approximate and log ε values not calculated.

system. No cobalt(III) product was obtained when the NaF had not been thoroughly dried. The deleterious effect of water is shown in the different electronic spectra obtained when $Co(hfa)_3$ is dissolved in solvents of varied water content.

Nuclear Magnetic Resonance.—Within the series of $Co(acac)_2L^+$ complexes, where L = en, tmed, bipy, and *o*-phen, the methyl resonance splittings increase in the ligand order listed. See Table I.

Improved instrumentation has now resulted in the observation of a slight splitting of the methyl proton signal in $Co(acac)_2en^+$ whereas a previous report[1] indicated a single sharp pmr signal. Even though the methyl groups are nonequivalent by symmetry, the slight differences mean that the effects which cause chemical shifts accidently cancel each other or that their magnitudes are very small. First of all, only very small ring currents,[24] if any,[25] are expected for the β-diketone and saturated diamine chelate rings. Furthermore, the small variation in Δ for different solvents (Table I) suggests that the solvent and ion-pair effects on both types of methyl groups are similar. These considerations suggest that the intramolecular effects (the differences expected from symmetry considerations) are not very large either.

The very slight splitting observed for the $Co(acac)_2en^+$ ion in three different solvents reinforces our earlier warning[1] that care must be taken in the assignment of a definite configuration to one of two or more isomers based on the lack of splitting of a pmr resonance peak. Even though symmetry considerations may imply differences, no splitting will be observed (1) if the intermolecular differences accidently compensate the intramolecular differences or (2) if both the intramolecular and intermolecular differences are too small to be observed.

The large separation between the chemical shifts for the two types of methyl groups in the *o*-phen and bipy complexes appears indicative of a ring current diamagnetic anisotropy coupled with smaller solvent and ion-pair effects. From molecular models the solvation and ion-pair differences of the methyl groups should be in the order tmed > *o*-phen ~ bipy > en, whereas the ring anisotropy effect should be in the order *o*-phen > bipy >> tmed ~ en since aromatic rings have large ring currents.[26] The *trans* methyl groups in $Co(acac)_2$-bipy$^+$ and $Co(acac)_2$-*o*-phen$^+$ lie almost above the π cloud of the nitrogen heterocycle and are shielded. The *cis* methyl groups would be deshielded as a result of lying in the plane of the heterocyclic ligand. In greement with experiment, the extra ring of *o*-phenanthroline should add to the difference between the *cis* and *trans* methyl group splittings. Models of the en and tmed complexes show that all four of the β-diketone methyl groups are widely separated from the unsubstituted en. However, the diketone methyl groups *trans* to each other in the tetramethylated diamine are in closer proximity with the N-methyl groups than are the *cis* diketone methyl groups in that complex. This steric difference suggests that although similar solvation and ion pairing of all four methyl groups could take place in the en complex, the environments of the *cis* and *trans* diketone methyl groups in the alkylated en complex are distinct.

Furthermore, models indicate that solvation and ion-pairing differences should also occur for the complexes containing the aromatic ligands. The extremely greater methyl signal separations suggest that the ring anisotropy effect is more important, but the relative contributions can only be approximated.

The β-diketone ring proton shows shifts consistent with earlier electronic[27] and solvent[28] effect studies.

The tris cobalt(III) complexes with the unsymmetrical diketone 2,2-dimethyl-3,5-hexanedione are capable

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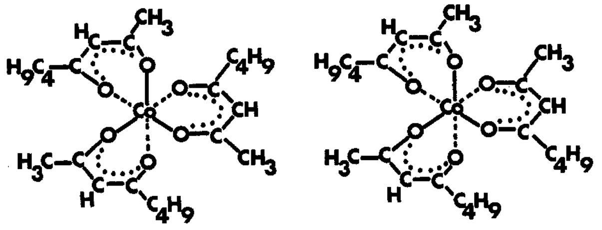
TABLE VI

VISIBLE AND ULTRAVIOLET SPECTRA OF TRIS(β-DIKETONE)COBALT(III) COMPLEXES[a]

Assignments	*fac*-Co(dhd)$_3$[b]	*mer*-Co(dhd)$_2$[b]	Co(thd)$_3$[b]	Co(hfa)$_3$[c]
$^1A_{1g} \rightarrow {}^1T_{1g}$	16,800 (2.13)	16,700 (2.12)	16,800 (2.16)	16,500 (2.08)
$^1A_{1g} \rightarrow {}^1T_{2g}$	24,500 sh, w[d]	22,800 sh, vw		23,000 sh
$t_{2g} \rightarrow \pi^*$	30,000 sh	30,000 sh	29,400 sh	29,000 sh
$\pi \rightarrow \pi^*$	33,400 sh	33,600 sh	32,800 sh	33,400 sh
$\pi \rightarrow \pi^*$	38,300 (4.44)	38,300 (4.50)	37,800 (4.69)	40,200 (4.48)
$\pi \rightarrow \pi^*$	43,100 (4.51)	43,100 (4.55)	42,800 (4.77)	42,900 sh

[a] All peak positions are given in cm^{-1}; log ϵ values are in parentheses. [b] Methanolic solutions. [c] Cyclohexane solutions. The spectra in dry tetrahydrofuran and dry CH_2Cl_2 are very similar with minor shifts in peak positions. [d] Shoulder; cm^{-1} values approximate and log ϵ not calculated; w, weak; vw, very weak.

of existing in two isomeric forms (Figure 3). One isomer has ligands coordinated so that the three methyl groups lie above an octahedral face (*fac*) while the other has three methyl groups above an octahedral meridian (*mer*). The *fac* and *mer* isomers of other unsymmetrical diketone complexes have been separated and characterized by Fay and Piper.[11,12] The *fac* isomer has a threefold axis of rotation; thus all three ligands are in equivalent environments. The *mer* isomer has no symmetry other than an identity element which means the three chelate rings are in nonequivalent environments. Therefore, a single methyl resonance, a single *t*-butyl resonance, and a single CH resonance should be observed for the *fac* isomer, while three distinct peaks for each type of proton should be observed for the *mer* isomer if the chemical shifts vary sufficiently for instrumental resolution. If the chemical shift differences are small, signal broadening might be the only indication of nonequivalence. Figure 2 (a and b) shows the spectra of the *fac* and *mer* isomers. The assignments of these signals are given in Table I and are based on intensities and comparison with the symmetrical Co(acac)$_3$ and Co(thd)$_3$ complexes. The splittings of the methyl and CH protons of the *mer* complex (Figure 2b) are evident using the normal sweep width of 500 cps whereas the *t*-butyl proton signal is a singlet and quite sharp. At a sweep width of 50 cps, however, a slight splitting into two peaks is observed in this signal (Figure 2c). Examination of a model of *mer*-Co(dhd)$_3$ indicates that the *trans t*-butyl groups are more exposed than the central *t*-butyl group. Thus the possibility of similar solvation patterns for the two *trans t*-butyl groups may account for the imperceptible splitting of two of the *t*-butyl groups.



fac **mer**

Figure 3.—The facial (*fac*) and meridional (*mer*) isomers of Co(dhd)$_3$.

Infrared, Visible, and Ultraviolet Spectra.—The infrared spectra of the two Co(dhd)$_3$ isomers indicate that structural identification from these data is unlikely. Based on the ^{18}O-labeled complexes investigated by Pinchas, *et al.*,[14] the C $\overset{\cdot\cdot\cdot}{-}$ O and C $\overset{\cdot\cdot\cdot}{-}$ C stretching assignments have been reversed to those recommended by Bailar and coworkers.[15,19,20] In general, the infrared spectra are as expected for the species prepared in this study.

The energy and shape of the electronic absorption bands of the two isomers of Co(dhd)$_3$ are also virtually identical and correspond well with the spectra of other tris-diketonato complexes.[11,12,21]

The *mer* isomer ultraviolet bands are more intense than the corresponding *fac* isomer absorptions as was observed by Fay and Piper[11] for tris(1,1,1-trifluoro-2,4-pentanedionato)cobalt(III) and tris(1-phenyl-1,3-butanedionato)cobalt(III).

Chemically the Co(hfa)$_3$ complex appears less stable than the corresponding acac, dhd, and thd complexes; however, the $^1A_{1g} \rightarrow {}^1T_{1g}$ (d ↔ d) transition of Co(hfa)$_3$ is only slightly below that observed for other cobalt(III) β-diketonates. The ultraviolet spectrum also shows only slight differences in the $\pi \rightarrow \pi^*$ and $t_{2g}^* \rightarrow \pi^*$ transitions. The inductive effect of the ligand CF_3 groups should weaken the O→Co σ bonding which in turn should give less π interaction. Apparently the π, π^*, t_{2g}^*, and e_g^* levels shift almost the same amount so that little change is observed in the spectrum of Co(hfa)$_3$. Most of the complexes appear to have a weak shoulder around 25,000 cm^{-1}, which is probably the $^1A_{1g} \rightarrow {}^1T_{2g}$ band, and another weak shoulder around 33,000 cm^{-1}, which has been assigned as one of the $\pi \rightarrow \pi^*$ components by Barnum.[21] Our previous studies[1a,2] and those of Boucher[3,19,20] have neglected these because of their weak shoulder obscureness.

The Co(acac)$_2$tmed$^+$ spectral transitions indicate that the methylated diamine has a low ligand field strength comparable to oxygen donors. The low field is not too surprising when the steric repulsions which occur in this species are considered.

Experimental Section

Acetylacetone and 2,2,6,6-Tetramethylheptane-3,5-dione.—Acetylacetone and 2,2,6,6-tetramethylheptane-3,5-dione were obtained commercially (Fisher and Pierce, respectively) and used without further purification.

Hexafluoroacetylacetone.—Commercial hexafluoroacetylacetone (Columbia) was dehydrated by shaking with two volumes of concentrated sulfuric acid. After three such extractions the hexafluoroacetylacetone was distilled and the fraction boiling at 67–68° was collected and stored under dry nitrogen.[29]

2,2-Dimethylhexane-3,5-dione.—2,2-Dimethylhexane-3,5-dione was prepared by modification of a previously published procedure.[30] Initially 54.0 g (1.00 mol) of sodium methoxide was suspended in 100 ml of anhydrous diethyl ether in a three-neck 1-l. flask fitted with an overhead stirrer, condenser, and dropping funnel. The suspension was stirred as 88 g (98 ml, 1.00 mol) of ethyl acetate was slowly added over a period of 1 hr, and stirring was maintained for 30 min after the complete addition of the acetate. To the tan suspension, 100 g (123 ml, 1.00 mol) of pinacolone was added slowly over a period of about 2 hr, and stirring was maintained for an additional 2 hr. The reddish brown suspension was allowed to stand 16 hr at room temperature without stirring, after which the tan solid was extracted from the suspension with 300–500 ml of ice water. The organic layer was further extracted with two 50-ml portions of cold water. The combined aqueous portions were acidified with 28 ml of concentrated H_2SO_4 (0.50 mol) in 100 ml of cold water. A yellow organic phase resulted which was separated from the aqueous layer and distilled twice. The fraction boiling at 170–174° was collected; yield, 14.0 g, 10%. *Anal.* Calcd for $C_8H_{14}O_2$: C, 67.60; H, 9.86. Found:[31] C, 67.40; H, 10.00.

Sodium Dinitrobis(acetylacetonato)cobaltate(III).—The complex was prepared and purified as previously described.[20]

Bis(acetylacetonato)(N,N,N′,N′-tetramethylethylenediamine)cobalt(III) Perchlorate.—Recrystallized sodium dinitrobis(acetylacetonato)cobaltate(III) (2.0 g, 5.4 mmol) was dissolved in 30 ml of water and 20 ml of methanol. Norit A carbon (1.5 g) and 0.63 g (5.4 mmol) of N,N,N′,N′-tetramethylethylenediamine were then added simultaneously to the solution of the complex. The solution was stirred for 15 min at room temperature and then filtered by suction. The carbon was washed with two 5-ml portions of methanol which were combined with the original filtrate. Then 15 g (110 mmol) of sodium perchlorate monohydrate in 15 ml of water was added to the solution which was kept at 0° for 3 hr. The solution was filtered and the resulting green crystals were washed with cold water and two 5-ml portions of ether before being air dried; yield, 0.7 g, 30%. The product was recrystallized by dissolution in a minimum amount of $CHCl_3$ and filtering any insoluble material. An equal volume of anhydrous ether was added to the filtrate and the solution was kept at 0° for 4 hr. The green product was filtered, washed with 10 ml of ether, and air dried; yield, 0.5 g, 20%. *Anal.* Calcd for $C_{16}H_{30}O_8N_2CoCl$: C, 40.61; H, 6.41; N, 5.92. Found: C, 40.49; H, 7.10; N, 5.99.

Bis(acetylacetonato)(1,10-phenanthroline)cobalt(III) Perchlorate.—Recrystallized sodium dinitrobis(acetylacetonato)cobaltate(III) (2.0 g, 5.4 mmol) was dissolved in 50 ml of water and 20 ml of methanol. Simultaneously 1.5 g of Norit A carbon and 0.99 g (5.4 mmol) of 1,10-phenanthroline monohydrate dissolved in 15 ml of methanol were added to the solution of the complex. The solution was stirred vigorously for 15 min at room temperature and was then filtered by suction. The carbon was washed with two 5-ml portions of methanol which were combined with the original filtrate. A solution of 0.9 g (7.3 mmol) of sodium perchlorate dissolved in 3 ml of water was then added, and a gray precipitate began forming immediately. After cooling in an ice bath the solution was filtered. The gray product was washed with cold water and ether and then was air dried; yield, 1.4 g, 49%. The product was recrystallized by dissolution in a minimum amount of boiling methanol and filtering while hot. The solution was allowed to cool and 10 ml of anhydrous ether was added. The gray-brown product was filtered and washed with methanol and ether and then air dried; yield, 0.6 g, 21%. *Anal.* Calcd for $C_{22}H_{22}O_8N_2CoCl$: C, 49.21; H, 4.14; N, 5.22. Found: C, 49.27; H, 4.81; N, 5.38.

Bis(acetylacetonato)(ethylenediamine)cobalt(III) Perchlorate and Bis(acetylacetonato)(2,2′-bipyridine)cobalt(III) Iodide.—These complexes had been retained from a previous investigation and were recrystallized before use by the published procedure.[2]

Tris(2,2,6,6-tetramethylheptane-3,5-dionato)cobalt(III).—First 5.7 g (13.4 mmol) of sodium hexanitrocobaltate(III) was dissolved in 25 ml of water and to this was added a solution of 1.6 g (40 mmol) of sodium hydroxide and 7.4 g (40 mmol) of 2,2,6,6-tetramethylheptane-3,5-dione in 50 ml of 50% ethanol. The solution was allowed to stand overnight at room temperature. The green precipitate was filtered from the solution by suction, washed with cold water and cold methanol, and then air dried. The product was further purified by washing with methanol on a sintered-glass filter until about one-fourth of the solid had dissolved and the washings no longer had a brown discoloration. Further purification was effected by vacuum sublimation at 100°; yield, 4.8 g, 58%; mp 260–261° (lit. mp 245°,[5] 260°[32]). *Anal.* Calcd for $C_{33}H_{57}O_6Co$: C, 65.24; H, 9.46; mol wt, 608. Found: C, 65.31; H, 9.33; mol wt, 609.

Tris(2,2-dimethylhexane-3,5-dionato)cobalt(III).—First 7.5 g (18.5 mmol) of sodium hexanitrocobaltate(III) was dissolved in 25 ml of water and to this was added a solution of 2.4 g (60 mmol) of sodium hydroxide and 8.5 g (60 mmol) of 2,2-dimethylhexane-3,5-dione in 25 ml of 50% ethanol. The solution was allowed to stand at room temperature for 48 hr by which time a large amount of green oil had appeared in the vessel. The oil was extracted from the aqueous solution with heptane. The compound was purified by chromatographing the concentrated heptane solution on a 30 cm × 4 cm column of silica gel. A green band characteristic of the tris species remained on the top portion of the column with very little movement. After washing with 500 ml of heptane and 500 ml of CH_2Cl_2, the tris complex was eluted with methanol. The methanol solution was evaporated and the resulting tacky solid was placed under vacuum. The mixture of *fac*- and *mer*-Co(dhd)$_3$ appears to pick up moisture rapidly in air; therefore, analyses of the mixture were made on samples which had been dried *in vacuo* (12 hr, 25°) and handled in a nitrogen (prepurified grade) atmosphere. *Anal.* Calcd for $C_{24}H_{39}O_6Co$; C, 59.77; H, 8.15; mol wt, 482. Found: C, 59.75; H, 8.19; mol wt, 460.

Separation of *fac*- and *mer*-Tris(2,2-dimethylhexane-3,5-dionato)cobalt(III).—The *fac* and *mer* isomers of tris(2,2-dimethylhexane-3,5-dionato)cobalt(III) were separated by thin layer chromatography using Silica Gel D-5 of 1-mm thickness on 20 cm × 20 cm glass plates. Concentrated carbon tetrachloride solutions of the mixed complex were placed on the plate and developed using CH_2Cl_2. Multiple development in the same solvent was sometimes necessary to achieve clean separation. The R_f values based on one development of approximately 15 cm are: *mer*, 0.25 ± 0.03; *fac*, 0.07 ± 0.03. The isomers were removed from the plate by scraping off the appropriate areas and extracting the complexes from the silica gel with methanol. The solid complexes were obtained by evaporating the methanol solutions and drying under vacuum. *Anal.* Calcd for *mer*-$C_{24}H_{39}O_6Co$: C, 59.77; H, 8.15. Found: C, 59.90; H, 8.15. Calcd for *fac*-$C_{24}H_{39}O_6Co$: C, 59.77; H, 8.15. Found: C, 59.75; H, 8.17.

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[31] Elemental analyses by Charles Meade, Director, University of Massachusetts Microanalytical Laboratory, and by Huffman Laboratories, Inc., Wheatridge, Colo.

[32] R. E. Sievers, private communication.

Tris(hexafluoroacetylacetonato)cobalt(III).—Initially 1.1 g (26 mmol) of powdered sodium fluoride, which had been dried at 110° for 3 hr followed by cooling under vacuum, was dissolved in 18.0 g (86.5 mmol) of hexafluoroacetylacetone which had been dehydrated as described above. One gram (8.7 mmol) of CoF_3 was added to the solution and after approximately 1 min of gentle swirling the solution turned dark green. The solution was kept at room temperature for 12 hr. All transfers and weighings were performed in a dry nitrogen glove bag and the reaction vessels were removed only when stoppered. The excess ligand was vacuum distilled from the solid at 25°. The dark green complex sublimed directly from the reaction vessel into an air-cooled glass column upon being heated to 45–50° in an oil bath; yield 2.6 g, 44%; mp 98–99° (lit. mp 93–94°,[8] 94–95°[9]). *Anal.* Calcd for $C_{15}H_3O_6CoF_{18}$: C, 26.47; H, 0.44; mol wt, 680. Found: C, 26.75; H, 0.60; mol wt, 775.[33]

Infrared Spectra.—All infrared spectra were obtained on a Beckman Model IR-10 infrared spectrophotometer. Potassium bromide disks of the solids were used for recording spectra while the spectra of the ligands were recorded neat between sodium chloride plates.

Visible–Ultraviolet Spectra.—The visible and ultraviolet spectra of all of the complexes were obtained with a Coleman Model EPS-3T Hitachi ratio recording spectrophotometer using methanolic solutions wherever possible in 1-cm cells. The spectra of $Co(hfa)_3$ were obtained in tetrahydrofuran and methylene chloride which had been dried over and distilled from CaH_2.

Proton Magnetic Resonance Spectra.—Proton magnetic resonance spectra were obtained with a Varian A-60 high-resolution spectrometer at 60 Mc using tetramethylsilane as an internal standard. The bis(acetylacetonato)(ethylenediamine)cobalt(III) perchlorate spectrum was also recorded by Varian Associates on a Varian HA-100 high-resolution spectrometer at 100 Mc in D_2O using tetramethylsilane as an external standard.

Molecular Weights.—Molecular weights of neutral complexes were obtained with a Mechrolab vapor-phase osmometer (Model 301A) with a 25° probe using reagent grade benzene solutions. The instrument was calibrated using benzene solutions of benzil.

Chromatographic Substrates.—For the column chromatography separation Silica Gel Woelm (M. Woelm, Eschwege, Germany) was used after presoaking in hexane. The thin layer chromatographic plates were prepared from aqueous suspensions of Silica Gel D-5 (Camag, Muttenz, Switzerland), dried at room temperature for 2–3 hr, and then dried at 100° for 4 hr.

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[33] The molecular weight was obtained in benzene in which the solubility of $Co(hfa)_3$ is low. The measurements were actually made at concentrations well below the accepted limits of the instrument.

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Rates of Substitution Reactions of Tetrakis(triethyl phosphite)metal(0) Compounds of the Nickel Triad

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The rate of ligand substitution between tetrakis(triethyl phosphite)nickel(0) and cyclohexyl isocyanide has been studied in *n*-hexane and benzene solutions by infrared spectroscopy. The reaction is first order in complex concentration and independent of the isocyanide concentration. The activation parameters are $\Delta H^{\ddagger} = 32$ kcal/mol and $\Delta S^{\ddagger} = +19$ eu in *n*-hexane solution and $\Delta H^{\ddagger} = 27$ kcal/mol and $\Delta S^{\ddagger} = +2$ eu in benzene. Tetrakis(triethyl phosphite)palladium(0) and tetrakis(triethyl phosphite)platinum(0) were prepared and the rates of ligand exchange between these complexes and free triethyl phosphite were studied in toluene solution by proton magnetic resonance. For both complexes the exchange reaction is first order in complex concentration and independent of the concentration of free phosphite. The activation parameters [$\Delta H^{\ddagger} = 22$ kcal/mol and $\Delta S^{\ddagger} = +30$ eu for the exchange reaction between $Pd[P(OC_2H_5)_3]_4$ and $P(OC_2H_5)_3$; $\Delta H^{\ddagger} = 26$ kcal/mol and $\Delta S^{\ddagger} = +24$ eu for the reaction between $Pt[P(OC_2H_5)_3]_4$ and $P(OC_2H_5)_3$] are compatible with a dissociative (SN1) mechanism. These results show that the activation energies for M–P bond rupture in the compounds $M[P(OC_2H_5)_3]_4$ vary in the order Ni > Pd < Pt.

Introduction

Complexes of zerovalent nickel, palladium, and platinum with phosphites or phosphines as ligands have been known for several years.[1] However, there is as yet no quantitative information on the M–P bond strengths in these systems. The experiments reported in this paper were carried out with the objective of studying the kinetics of ligand exchange or ligand substitution reactions for the nickel triad series of $M[P(OC_2H_5)_3]_4$ and to obtain data on the M–P bond dissociation energy.

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