intensity of the main line) and is lost in the base line. If a hidden higher binding energy peak were comparable in intensity to that of the lower binding energy peak, then the Ru $3d_{5/2}$ intensity derived from the deconvoluted spectrum shown in Figure 1 would be anomalously low compared with that of other complexes while the C 1s line intensity would be anomalously high. Furthermore, the large Ru 3d splitting required to hide the high-binding-energy Ru 3d peak under the C 1s line ought to be observable even in the Ru $2p_{3/2}$ spectrum of the complex. We examined these possibilities by comparing Ru $3d_{5/2}$/Cl 2p and Ru $2p_{3/2}$/Cl 2p intensity ratios recorded for **7** with those of all the other ruthenium chloride complexes. The Ru $3d_{5/2}$/Cl 2p and Ru $2p_{3/2}$/Cl 2p intensity ratios for **7** are both within 20% (albeit on the *low* side of all but one) of all other measured ratios. The Ru $2p_{3/2}$ line width for **7** is normal. Given experimental errors, we find then that at least 80% of the Ru $3d_{5/2}$ intensity expected from two ruthenium centers in **7** is accounted for in the deconvoluted spectrum. Consequently, the metal XP spectrum of **7** is consistent with that of a strongly delocalized class III complex. For such a complex a large portion of the total metal core level photoemission intensity resides in a single, low-binding-energy line. From the quality of the spectrum we estimate, using eq 2, that the electron exchange parameter α for **7** must be greater than 0.9.

Conclusions

The diruthenium complexes examined have provided the opportunity to systematically assess the effects of ligand coordination environment, metal oxidation state, and metal-metal interaction on the metal XP spectra. One complex is of particular interest in this series; the symmetric, mixed-valence [Ru(II),Ru(III)] complex $[As(p\text{-tol})_3]_2ClRuCl_3RuCl[As(p\text{-tol})_3]_2$. Depending on the strength of the metal-metal interaction, the metal XP spectrum from this complex could give any results along the continuum from two equally intense metal lines separated by 1 eV or more, to unequal intensities from the two lines with the lower binding energy line "stealing" intensity from the higher binding energy line, to a single, narrow metal line (indistinguishable metal centers). The spectrum observed is a function of the extent of unpaired electron delocalization during photoemission. It was found that, to the degree of resolution possible, this complex gives a metal spectrum in which at least 80% of the metal signal is present in a single, low-binding-energy final state. This experimental result reflects more extensive unpaired electron delocalization in this complex compared with that in the Creutz-Taube complex $[(NH_3)_5Ru(pz)Ru(NH_3)_5]^{5+}$, which gives two well-separated metal lines of equal intensity. We estimate the value of α in **7** is greater than 0.9, whereas in the Creutz-Taube complex it is less than 0.10. This work, combined with Hush's theory, suggests that very unusual metal XP spectra ought to be obtained from class III mixed-valence complexes having metal-metal spacings between 3.5 and 6 Å.

Acknowledgment. P.B. wishes to thank Exxon Chemical Co. for permission to publish this work.

Contribution from the Faculty of Chemistry,
University of Thessaloniki, Thessaloniki 54006, Greece

Spectral Study of Tris(β-dionato)cobalt(III) Chelates. Structure-Redox Potential Relations

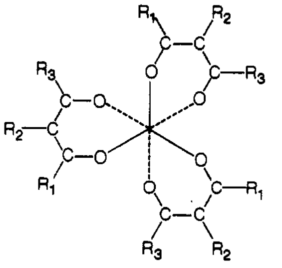
Chris Tsiamis,* Stavros Cambanis, and Chris Hadjikostas

Received March 21, 1986

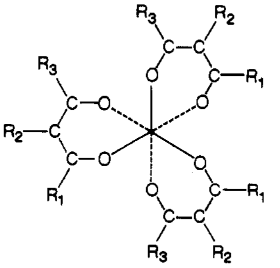
A series of 16 tris(β-dionato)cobalt(III) chelates have been prepared, and their infrared and solution electronic spectra were obtained. Evidence is provided that substituents within the β-dionato moiety induce electronic effects influencing the electronic structure, bonding characteristics, and stability of these complexes while they barely affect the ligand field parameter *Dq*. The influence of the substituents on the chelate ring electron density is primarily inductive in nature, and the parameters best describing this influence are Hammett σ functions. It was found that electron-attracting groups weaken the Co—O bond and strengthen the $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ bonds in the chelate ring, the stretching frequencies of which are linearly dependent on Hammett σ functions. Similarly dependent are the polarographic reduction potentials of these low-spin chelates and the energies of the frontier molecular orbitals. The experimentally determined energies of the HOMO and LUMO orbitals are in excellent agreement with previously computed values. The linear dependence encompasses the energy of the first charge-transfer transition assigned to a $\pi^* \leftarrow t_{2g}$ excitation.

Introduction

The chelates of β-dione compounds constitute a very important class of complexes. Their tremendous versatility is attested to by the fact that they have been coordinated to a great variety of metals and metalloids.[1-3] Coordination takes place through the carbonyl oxygen atoms, and with trivalent metals the oxygen may be thought of as occupying the apices of a slightly distorted octahedron.[4] The symmetric β-diketones afford optical isomers[5] whereas Claisen condensation offers the possibility of forming asymmetric β-dione compounds that can be used for the preparation of geometrical isomers (facial and meridional) in addition to the optical isomers.[4,6] The number of such compounds can be extended even more to encompass complexes with specific groups since the β-diketonato chelates exhibit "quasi-aromatic" character and many electrophilic substitution reactions have been effected at the methinic carbon atom of the chelate ring.[7,8] In this way a series of complexes can be prepared in order to investigate the influence of various substitutents on the spectral characteristics and other physical properties of this class of compounds.[9,10]



facial (*fac*)



meridional (*mer*)

---

(1) Fackler, J. P., Jr. *Prog. Inorg. Chem.* **1967**, *7*, 361.
(2) Thomson, D. W. *Struct. Bonding (Berlin)* **1971**, *9*, 27.
(3) Joshi, K. C.; Pathak, V. N. *Coord. Chem. Rev.* **1977**, *22*, 37.
(4) Fay, R. C.; Piper, T. S. *J. Am. Chem. Soc.* **1962**, *84*, 2303.
(5) Moshier, R. W.; Sievers, R. E. *Gas Chromatography of Metal Chelates*; Pergamon: London, 1965.
(6) Fay, R. C.; Piper, T. S. *J. Am. Chem. Soc.* **1963**, *85*, 500.
(7) Collman, J. P. *Angew. Chem.* **1965**, *77*, 154 and references therein.
(8) Fackler, J. P., Jr. *J. Chem. Soc.* **1957**, 1962.

0020-1669/87/1326-0026$01.50/0

Table I. Nomenclature and Abbreviations for the Tris(1,3-dionato)cobalt(III) Chelates Studied

compd	R_1	R_2	R_3	full name	mp/°C (lit. mp/°C)
$Co(bdo)_3$ (**1**)	H	H	CH_3	tris(1,3-butanedionato)cobalt(III)	*fac* 160–161 (160),[a] *mer* 165–166 (165)[a][22]
$Co(ppdo)_3$ (**2**)	C_6H_5	H	H	tris(1-phenyl-1,3-propanedionato)cobalt(III)	183–185
$Co(bpdo)_3$ (**3**)	H	H	$C(CH_3)_3$	tris(4,4-dimethyl-1,3-pentanedionato)cobalt(III)	*fac* 117–119, *mer* 121–123
$Co(acac)_3$ (**4**)	CH_3	H	CH_3	tris(2,4-pentanedionato)cobalt(III)	219–220 (220)[a][23]
$Co(bzac)_3$ (**5**)	C_6H_5	H	CH_3	tris(1-phenyl-1,3-butanedionato)cobalt(III)	213–214 (213)[a][4]
$Co(bbdo)_3$ (**6**)	CH_3	H	$C(CH_3)_3$	tris(5,5-dimethyl-2,4-hexanedionato)cobalt(III)	131–133
$Co(tfac)_3$ (**7**)	CF_3	H	CH_3	tris(1,1,1-trifluoro-2,4-pentanedionato)cobalt(III)	*fac* 128–129 (129–129.5), *mer* 159 (158–158.5)[6]
$Co(dbmo)_3$ (**8**)	C_6H_5	H	C_6H_5	tris(1,3-diphenyl-1,3-propanedionato)cobalt(III)	252–253
$Co(bztfo)_3$ (**9**)	C_6H_5	H	CF_3	tris(1-phenyl-4,4,4-trifluoro-1,3-butanedionato)cobalt(III)	192–192.5
$Co(bzpmo)_3$ (**10**)	C_6H_5	H	$C(CH_3)_3$	tris(1-phenyl-4,4-dimethyl-1,3-pentanedionato)cobalt(III)	219–221
$Co(hfac)_3$ (**11**)	CF_3	H	CF_3	tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)cobalt(III)	101–102
$Co(dpmo)_3$ (**12**)	$C(CH_3)_3$	H	$C(CH_3)_3$	tris(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III)	245–246 (245)[a][24]
$Co(3\text{-}NO_2\text{-}acac)_3$ (**13**)	CH_3	NO_2	CH_3	tris(2-nitro-2,4-pentanedionato)cobalt(III)	198–199 (198)[a][25]
$Co(3\text{-}SCN\text{-}acac)_3$ (**14**)	CH_3	SCN	CH_3	tris(2-thiocyano-2,4-pentanedionato)cobalt(III)	166–167 (166–167)[a][26]
$Co(2\text{-}NO_2\text{-}bpdo)_3$ (**15**)	H	NO_2	$C(CH_3)_3$	tris(2-nitro-4,4-dimethyl-1,3-pentanedionato)cobalt(III)	*fac* 140–141, *mer* 147–149
$Co(2\text{-}SCN\text{-}bpdo)_3$ (**16**)	H	SCN	$C(CH_3)_3$	tris(2-thiocyano-4,4-dimethyl-1,3-pentanedionato)cobalt(III)	*fac* 123–125, *mer* 131–133

[a] Decomposes.

The important role the substituents play in the electronic structure of the β-onato metal chelates is demonstrated by changes in the spectra of these compounds. Nakamoto and co-workers[11,12] studying the vibrational spectra of 1,3-diketonato metal chelates recognized the influence of the substituents on group frequencies and attributed the observed shifts to electronic effects. Electronic effects engendered by substitutents far away from the coordination site were also invoked[9] to account for the large spectral shifts in the charge-transfer bands. Such behavior is not uncommon among transition-metal complexes. Ford and co-workers[13] have found that in a series of $Ru(NH_3)_5(py\text{-}X)^{2+}$ complexes the energy of the first metal-to-ligand charge-transfer band, MLCT, correlates linearly with the Hammett σ_p function of the substituent X attached to the coordinated pyridine. In addition the MLCT energy showed[13,14] linear dependence on the half-wave reduction potential of the free ligand (py-X). Similar dependence was established in many other complexes of ions with d^6 electronic configuration.[14-17]

The complexes of β-diones are eminently suitable for studies aimed at testing the extent of the validity of such findings. Independent investigators have established that good correlation obtains between the Hammett σ function and the polarographic reduction potential of these complexes.[18-20] Furthermore, it was suggested[21] that spectroscopically derived parameters might also correlate with Hammett σ functions. The least studied series of this class, the tris(1,3-diketonato)cobalt(III) chelates, attracts particular interest in view of the d^6 configuration of the central ion. These complexes are easily prepared and purified.

The present study was undertaken in order to investigate (a) the electronic interactions of the substituents with the chelate ring, (b) the changes incurred in group vibrations, (c) the shifts induced in spectral bands, and (d) the alterations effected in electron distribution in the ground state and to seek correlations between experimentally determined or derived quantities and parameters depicting the electronic interactions engendered by the substitutents. Accordingly, a series of 16 tris(1,3-dionato)cobalt(III) complexes were prepared, their infrared and electronic spectra were recorded, and their polarographic reduction potentials were determined. The compounds studied are listed in Table I.

Experimental Section

Synthesis of Ligands. The ligands Hhfac, Htfac, Hacac, Hbzac, Hbztfo, Hdpmo, and Hdbmo were obtained commercially. The sodium salts of the other β-dione compounds were synthesized by the Claisen condensation according to the methods described by Collman[27] and by Yamakawa and Kaneoya[22] with minor modifications.

Preparation of Tris(β-dionato)cobalt(III) Complexes. The method of Bauer and Drinkard[23] and that of Fay and Piper[4,6] were employed for the preparation of the tris(1,3-onato)cobalt(III) chelates. The 2-substituted derivatives were obtained by the method first described by Collman and co-workers.[7] The compounds were purified by column chromatography on Al_2O_3 with a 1:1 benzene–dichloromethane mixture as eluent. Trituration with ethanol gave samples rich in facial isomers.[4,6]

Electronic Spectra. The spectra in the region 200–1400 nm were recorded in chloroform, benzene, and acetonitrile at 25 °C with a Cary 17D spectrophotometer. In acetonitrile solutions a slight decomposition of the complexes with fluorinated ligands was observed. Since no other spectral shifts were observed in these solvents, within experimental error, it was concluded that there is no solvent dependence. Therefore, only the band maxima obtained in chloroform solution are reported here. The reproducibility of the ϵ values in chloroform were found in general to be within 8%.

Infrared Spectra. The infrared spectra in the region 4000–300 cm^{-1} were recorded on a Perkin-Elmer 467 spectrophotometer. The KBr matrix method was employed for the preparation of the sample. Wavenumber calibration was made with polystyrene film and with 1,2,4-trichlorobenzene.

Electrochemical Measurements. Electrochemical data were obtained in acetonitrile solutions by conventional polarography and cyclic voltammetry. The supporting electrolyte was maintained at 0.10 M with tetraethylammonium perchlorate, TEAP. Potential values were measured vs. the SCE (NaCl) electrode and refer to one-electron reversible or nearly reversible one-electron processes indicated by the $E_{3/4} - E_{1/4}$ values. Cyclic voltammograms were obtained with Hg as well as carbon-fiber electrodes with a Pt wire as auxiliary electrode. Further details are given elsewhere.[19,20]

---

(9) Lintvedt, R. L. In *Concepts of Inorganic Photochemistry*; Adamson, A. W., Fleischauer, P. D., Eds.; Wiley: New York, 1975; p 299.

(10) Mehrotra, R. C.; Bohra, R.; Gauer, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic: London, 1978.

(11) Nakamoto, K.; Morimoto, Y.; Martell, A. E. *J. Phys. Chem.* **1962**, *66*, 346 and references therein.

(12) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd Ed.; Wiley: New York, 1978.

(13) (a) Ford, P. C.; Rudd, D. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187. (b) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1977**, *99*, 7213.

(14) Johnson, C. R.; Shepherd, R. E. *Inorg. Chem.* **1983**, *22*, 2439.

(15) Figard, J. E.; Petersen, J. D. *Inorg. Chem.* **1978**, *17*, 1059.

(16) Hrepic, N. V.; Malin, J. N. *Inorg. Chem.* **1979**, *18*, 409.

(17) Juris, A.; Belser, P.; Barigelleti, F.; von Zelewsky, A.; Balzani, V. *Inorg. Chem.* **1986**, *25*, 256.

(18) Lintvedt, R. L.; Russel, H. D.; Holtzclaw, H. F., Jr. *Inorg. Chem.* **1966**, *5*, 1603.

(19) Jannakoudakis, A. D.; Tsiamis, C.; Jannakoudakis, P. D.; Theodoridou, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1985**, *184*, 123.

(20) Tsiamis, C.; Michael, C.; Jannakoudakis, A. D.; Jannakoudakis, P. D. *Inorg. Chim. Acta* **1986**, *120*, 1.

(21) Fatta, A. M.; Lintvedt, R. L. *Inorg. Chem.* **1971**, *10*, 478.

(22) Yamakawa, K.; Kaneoya, H. *Chem. Pharm. Bull.* **1976**, *24*, 1902.

(23) Bauer, H. F.; Drinkard, W. C. *J. Am. Chem. Soc.* **1960**, *82*, 5031.

(24) Hammond, G. S.; Nonhebel, D. C.; Wu, C. S. *Inorg. Chem.* **1963**, *2*, 73.

(25) Collman, J. P.; Marshall, R. L.; Young, W. L.; Goldby, S. D. *Inorg. Chem.* **1962**, *1*, 704.

(26) Collman, J. P.; Marshall, R. L.; Young, W. L.; Sears, C. T., Jr. *J. Org. Chem.* **1963**, *28*, 1449.

(27) Collman, J. P.; Kittleman, E. T.; Hurt, W. S.; Moore, N. A. *Inorg. Synth.* **1965**, *8*, 144.

Table II. Wavenumbers (cm^{-1}) of the C$\overset{\cdots}{-}$O, C$\overset{\cdots}{-}$C, and Co—O Stretching Vibrations and C–H In-Plane and Out-of-Plane Bend as well as Other Bands of Interest in a Series of Tris(1,3-dionato)cobalt(III) Chelates

	ν(C$\overset{\cdots}{-}$O)	ν(C$\overset{\cdots}{-}$C)	ν(Co—O)	ν(C—H)[a]	ν(C—H)[b]
Co(bdo)$_3$ (**1**)	1600	1520	495 (*mer*) 480 (*fac*)	1230	770
Co(ppdo)$_3$ (**2**)	1590	1560	490 (*mer*) 470 (*fac*)	1265	760
Co(bpdo)$_3$ (**3**)	1600	1510	500 (*mer*) 460 (*fac*)	1165	770
Co(acac)$_3$ (**4**)	1580	1530	465	1195	790
Co(bzac)$_3$ (**5**)	1585	1550	480 (*mer*) 470 (*fac*)	1210	760
Co(bbdo)$_3$ (**6**)	1580	1565	500 (*mer*) 475 (*fac*)	1170	768
Co(tfac)$_3$ (**7**)	1600	1540	445 (*mer*) 420 (*fac*)	1150	790
Co(dbmo)$_3$ (**8**)	1600	1550	485	1235	730
Co(bztfo)$_3$ (**9**)	1600	1570	440	1155	770
Co(bzpmo)$_3$ (**10**)	1610	1560	515 (*mer*) 470 (*fac*)	1180	775
Co(hfac)$_3$ (**11**)	1640	1620	430	1150	810
Co(dpmo)$_3$ (**12**)	1575	1535	460	1185	785
Co(3-NO$_2$-acac)$_3$ (**13**)	1570		470	1520[c]	1330[d]
Co(3-SCN·acac)$_3$ (**14**)	1560		475	2150[e]	
Co(2-NO$_2$-bpdo)$_3$ (**15**)	1590		530 (*mer*) 500 (*fac*)	1520[c]	1320[d]
Co(2-SCN-bpdo)$_3$ (**16**)	1585		540 (*mer*) 500 (*fac*)	2170[e]	

[a] In-plane bend. [b] Out-of-plane bend. [c] $\nu_{as}(NO_2)$. [d] $\nu_s(NO_2)$. [e] ν(C≡N).

Results

The formulas of the compounds prepared for the present investigation are given in Table I together with their melting points. The procedures employed in their preparation were similar to those reported in the literature. The reaction of the chelates of 1,3-ketoaldehydes with electrophilic reagents resulted invariably in 2-substitution even though the hydrogen in the 1-position is available for replacement. Efforts to insert substituents in the 2-position in the fluorinated Co(tfac)$_3$ and Co(hfac)$_3$ were unsuccessful as were the attempts to carry out electrophilic substitution reactions in Co(dpmo)$_3$, which has the bulky –C(CH$_3$)$_3$ groups in positions 1 and 3. The insertion of substituents in the 2-position of the tris(4,4-dimethyl-1,3-pentanedionato)cobalt(III), Co(bpdo)$_3$, although in low yield, indicated that, under the experimental conditions described, the steric inhibition apparently exercised effectively by the –C(CH$_3$)$_3$ groups in Co(dpmo)$_3$ is not sufficient to impede the replacement of the methinic hydrogen by various groups. The characterization of the complexes not previously known was based on the results of elemental analyses and standard spectroscopic methods.

Coordination of the β-dione ligands takes place through the carbonyl oxygen atoms. Nakamoto and co-workers[11] have produced evidence that in addition to the changes in frequency of the C═O and C═C vibrational modes induced by the formation of metal–oxygen bonds, there are frequency shifts engendered by the substituents attached to the carbonyl carbon atoms. Table II shows that the "metal-sensitive" Co—O band[28] is also affected by the substituents since there is no change in the central atom and appears at lower frequencies in the facial isomers.[4,6] The assignment of bands to C═O and C═C stretching vibrations is that proposed by Bellamy and Branch[29] since Pinchas and co-workers[30] provided irrefutable experimental evidence against suggestions based on theoretical calculations reversing the assignments.[12]

Of interest are the bands appearing at about 1200 and 800 cm^{-1}, attributed to the in-plane and out-of-plane bending vibrations, respectively, of the methinic C-H bond. As expected, in the 2-substituted derivatives these bands disappear. This and the appearance of characteristic group frequencies are clear indications of the formation of the desired products. Another consequence of 2-substitution is the merging of the bands attributed to C═O and C═C bonds.

Table III. Values of Hammett σ Constants

	R						
	H	CH$_3$	C(CH$_3$)$_3$	C$_6$H$_5$	CF$_3$	NO$_2$	SCN
σ_m	0.0	–0.07	–0.12	0.22	0.41	0.71	
σ_p	0.0	–0.17	–0.20	0.01	0.55	0.78	0.70

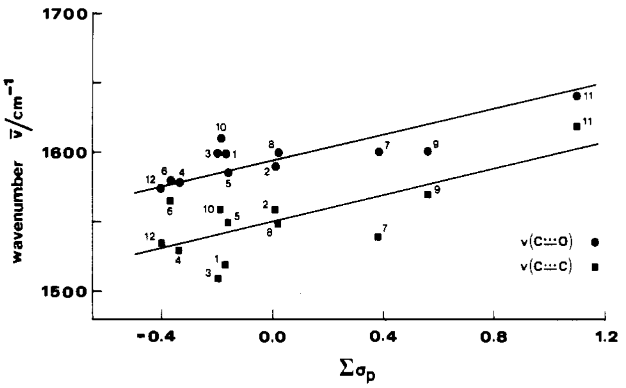


Figure 1. Plot of the ν(C$\overset{\cdots}{-}$O) and ν(C$\overset{\cdots}{-}$C) wavenumbers against the sum of the Hammett σ functions of the substituents.

From Table II it can be seen that electron-donating substituents in both the 1- and 3-positions cause a shift of the C═O and C═C stretching vibrations toward lower frequency while the reverse is true of the electron-attracting groups in the same positions. The direction and extent of the frequency shifts suggest that these might be due to electronic interactions engendered by the substituents. It is well-known that the carbonyl group is very sensitive to both resonance and inductive effects. Insofar as the Hammett σ functions are measures of changes in electron density, the possibility is raised of an approximately linear relationship between the frequency shifts and the sum of substituent σ constants. Hammett σ constants[31] for the substituent groups existing in the complexes investigated are given in Table III. Least-squares regression analysis indicated that there is good correlation between

---

(28) Fleming, C. A.; Thornton, D. A. *J. Mol. Struct.* **1973**, *17*, 79.
(29) Bellamy, L. J.; Branch, R. F. *J. Chem. Soc.* **1954**, 4491.
(30) Pinchas, S.; Silver, B. L.; Laulicht, I. *J. Chem. Phys.* **1967**, *46*, 1506.
(31) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

Table IV. Band Maxima Due to d–d Transitions and Ligand Field Parameters of Tris(1,3-dionato)cobalt(III) Complexes

compd	substituent R_1	R_2	R_3	$\bar{\nu}_1/\mu m^{-1\,a}$ $^3T_{1g} \leftarrow {}^1A_{1g}$	$\bar{\nu}_2/\mu m^{-1\,a}$ $^3T_{2g} \leftarrow {}^1A_{1g}$	$\bar{\nu}_3/\mu m^{-1\,b}$ $^1T_{1g} \leftarrow {}^1A_{1g}$	$\bar{\nu}_4/\mu m^{-1}$ $^1T_{2g} \leftarrow {}^1A_{1g}$	$10Dq/\mu m^{-1}$	$B/$ cm^{-1}	$C/$ μm^{-1}	$C/$ B
Co(bdo)$_3$ (**1**)	H	H	CH_3	0.900	1.205	1.690 (2.12)		1.99	430	0.380	8.8
Co(ppdo)$_3$ (**2**)	C_6H_5	H	H	0.875	1.205	1.675 (2.23)		1.96	420	0.380	8.3
Co(bpdo)$_3$ (**3**)	H	H	$C(CH_3)_3$	0.845	1.200	1.685 (2.20)		1.98	495	0.400	8.0
Co(acac)$_3$ (**4**)	CH_3	H	CH_3	0.925	1.220	1.685 (2.18)	2.500	1.98	425	0.365	9.0
Co(bzac)$_3$ (**5**)	C_6H_5	H	CH_3	0.885	1.205	1.670 (2.24)	2.440	1.96	445	0.375	8.4
Co(bbdo)$_3$ (**6**)	CH_3	H	$C(CH_3)_3$	0.850	1.215	1.675 (2.22)		1.94	520	0.385	7.4
Co(tfac)$_3$ (**7**)	CF_3	H	CH_3	0.915	1.205	1.665 (2.16)	2.420	1.96	395	0.360	9.1
Co(dbmo)$_3$ (**8**)	C_6H_5	H	C_6H_5	0.875	1.175	1.655 (2.36)	2.500	1.96	415	0.375	9.1
Co(bztfo)$_3$ (**9**)	C_6H_5	H	CF_3	0.875	1.170	1.645 (2.28)		1.94	405	0.370	9.1
Co(bzpmo)$_3$ (**10**)	C_6H_5	H	$C(CH_3)_3$	0.845	1.190	1.670 (2.21)		1.96	485	0.390	8.1
Co(hfac)$_3$ (**11**)	CF_3	H	CF_3	0.905	1.190	1.650 (2.14)	2.250	1.94	390	0.360	9.1
Co(dpmo)$_3$ (**12**)	$C(CH_3)_3$	H	$C(CH_3)_3$	0.845	1.225	1.690 (2.28)	2.410	1.96	550	0.395	7.2
Co(3-NO$_2$-acac)$_3$ (**13**)	CH_3	NO_2	CH_3	0.925	1.240	1.720 (2.34)		2.02	440	0.380	8.7
Co(3-SCN-acac)$_3$ (**14**)	CH_3	SCN	CH_3	0.925	1.240	1.710 (2.34)		2.00	435	0.375	8.6
Co(2-NO$_2$-bpdo)$_3$ (**15**)	H	NO_2	$C(CH_3)_3$	0.850	1.245	1.720 (2.18)		1.99	565	0.405	7.2
Co(2-SCN-bpdo)$_3$ (**16**)	H	SCN	$C(CH_3)_3$	0.850	1.240	1.720 (2.18)	2.410	1.99	560	0.405	7.3

[a] The extinction coefficient in the spin-forbidden transitions is $\epsilon \simeq 2$ mol^{-1} dm^3 cm^{-1}. [b] log (ϵ/mol^{-1} dm^3 cm^{-1}) in parentheses.

the carbonyl stretching frequency and the Hammett σ_p functions (Pearson's correlation coefficient $r = 0.99$). Figure 1 illustrates the relationship between $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ and $\sum \sigma_p$. Since the carbonyl carbon atom participates in the partially carbon–carbon double bond, the influence of the substituents should also be evident in the corresponding stretching vibrations. Indeed, the frequency shifts of the $\mathrm{C}\overset{\cdots}{-}\mathrm{C}$ stretching vibration parallel those in the $\mathrm{C}\overset{\cdots}{-}\mathrm{O}$ bond (Figure 1).

The carbonyl oxygen atoms surrounding the cobalt(III) ion impose a ligand field with geometry slightly deviating from octahedral.[6] The slight distortion hardly affects the local symmetry, which, for the assignment of spectral bands in solution, can be safely assumed to be octahedral although the molecular symmetry is significantly lower. This and the fact that the tris(1,3-diketonato)cobalt(III) chelates are diamagnetic imply that the ground state of the low-spin d^6 cobalt(III) ion is the uncomplicated $^1A_{1g}$ state. On this basis the electronic absorption spectra of the tris(1,3-dionato)cobalt(III) chelates are readily interpretable. Their main features in chloroform solution are shown in Figure 2, and the spectral data related to the ligand field transitions are summarized in Table IV. The spectral assignments are based on the energy level splittings originally proposed by Barnum[32] and adopted by other investigators.[9] The low extinction coefficient of the two bands in the near-infrared region is a clear indication of the spin-forbidden nature of these transitions.

The energies of the above d–d transitions in terms of the ligand field parameter $10Dq$ and the interelectronic repulsion parameters B and C are given by the well-known equations (1)–(4).[33]

$$\bar{\nu}_1' = E(^3T_{1g} \leftarrow {}^1A_{1g}) = 10Dq - 3C + 50B^2/10Dq \qquad (1)$$

$$\bar{\nu}_2' = E(^3T_{2g} \leftarrow {}^1A_{1g}) = 10Dq + 8B - 3C + 14B^2/10Dq \qquad (2)$$

$$\bar{\nu}_1 = E(^1T_{1g} \leftarrow {}^1A_{1g}) = 10Dq - C + 86B^2/10Dq \qquad (3)$$

$$\bar{\nu}_2 = E(^1T_{2g} \leftarrow {}^1A_{1g}) = 10Dq + 16B - C + 2B^2/10Dq \qquad (4)$$

The term $kB^2/10Dq$ expresses the configuration interaction in which has tacitly been assumed that $4.8B = C$.[34] Solution of the above equations is achieved by adopting the approximation that the term arising from configuration interaction $kB^2/10Dq$ is negligible and therefore can be ignored. Thus the parameters B and C may be estimated by taking the energy differences

$$\bar{\nu}_2' - \bar{\nu}_1' \simeq 8B \qquad (5)$$

$$\bar{\nu}_1 - \bar{\nu}_1' \simeq 2C \qquad (6)$$

From Table IV it is deduced that in the present series of cobalt(III) chelates the ratio C/B is about 9, that is twice the value obtained from the free ion parameters C and B.

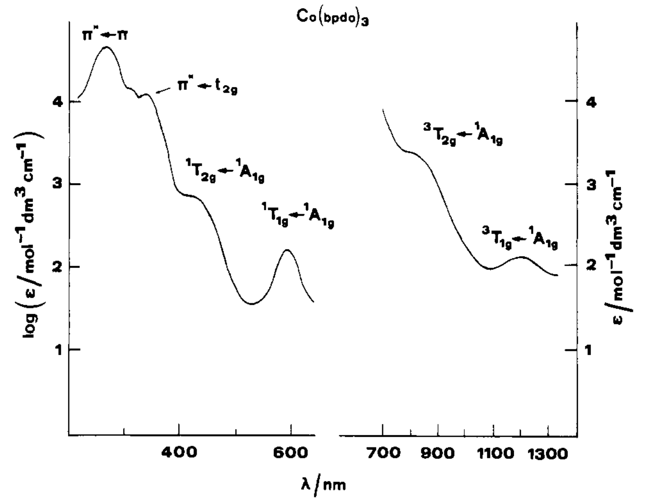


Figure 2. Electronic absorption spectrum of Co(bpdo)$_3$ in chloroform.

In order to achieve self-consistency, eq 1–3 were solved by iterative methods. Tentative values for $10Dq$ were obtained by using Jørgensen's[35] relationship $10Dq = f$(ligand) g(metal). The values of f(ligand) used were those reported in the literature[36] for the chromium(III) complexes of the same ligands. The value of g(Co(III)) was taken as 1.90 μm^{-1}.[37] The values of B and C were estimated by employing eq 5 and 6. The parameters $10Dq$, B, and C were then varied until the calculated values of the transitions agreed reasonably with the observed ones for each compound studied. The results are given in Table IV.

The parameter Dq in these series varies only slightly. Similar behavior of the β-diketone ligands was observed by Lintvedt and co-workers[21,36,38] in the case of the corresponding chromium(III) and iron(III) chelates. Although the influence of the substituents is barely noticeable in the splitting of the d orbitals caused by the β-dione moiety, their influence in the expansion of these orbitals, termed the nephelauxetic effect, is very much in evidence. Indeed, the values of the interelectronic repulsion parameters B and C are not only much lower than the corresponding free ion values (B = 1115 cm^{-1}, C = 4366 cm^{-1})[39] but also vary considerably along the series. Such variation was observed in the case of similar complexes of chromium(III) and iron(III). However, there are

---

(32) Barnum, D. W. *J. Inorg. Nucl. Chem.* **1961**, *21*, 221; **1961**, *22*, 183.

(33) Jørgensen, C. K. *Discuss. Faraday Soc.* **1958**, *26*, 110.

(34) Tanabe, Y.; Sugano, S. *J. Phys. Soc. Jpn.* **1954**, *9*, 753, 766.

(35) Jørgensen, C. K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon: Oxford, England, 1962.

(36) Lintvedt, R. L.; Kernitsky, L. K. *Inorg. Chem.* **1970**, *9*, 491.

(37) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; p 221.

(38) Fatta, A. M.; Lintvedt, R. L. *Inorg. Chem.* **1972**, *11*, 88.

(39) Griffith, J. S. *The Theory of Transition-Metal Ions*; Cambridge University Press: Cambridge, England, 1971; p 311.

Table V. Transitions Observed in the 2.4–4.0-μm^{-1} Region, $E_{1/2}$ Reduction Potentials, and Hammett $\sum\sigma$ Functions for the Tris(1,3-dionato)cobalt(III) Chelates Studied

	$\pi^* \leftarrow t_{2g}/\mu m^{-1}$ [a]	$CT/\mu m^{-1}$	$\pi^* \leftarrow \pi/\mu m^{-1}$		$E_{1/2}/V$	$\sum\sigma$
Co(bdo)$_3$ (**1**)	3.010 (3.89)	3.300 (4.05)		3.845 (4.55)	−0.32	−0.17
Co(ppdo)$_3$ (**2**)	2.770 (4.20)	3.125 (4.38)	3.510 (4.81)	3.685 (4.82)	−0.19	+0.01
Co(bpdo)$_3$ (**3**)	2.930 (3.88)	3.250 (4.09)		3.800 (4.62)	−0.28	−0.20
Co(acac)$_3$ (**4**)	3.080 (3.96)	3.390 (4.11)		3.860 (4.61)	−0.34	−0.34
Co(bzac)$_3$ (**5**)	2.795 (4.16)	3.335 (4.61)	3.520 (4.81)	3.845 (4.84)	−0.21	−0.16
Co(bbdo)$_3$ (**6**)	2.965 (3.86)	3.310 (4.10)		3.815 (4.51)	−0.38	−0.37
Co(tfac)$_3$ (**7**)	2.420 (3.00)	3.010 (3.86)	3.425 (4.22)	3.920 (4.62)	+0.05	+0.38
Co(dbmo)$_3$ (**8**)	2.650 (4.40)	3.175 (4.74)	3.415 (5.01)	3.675 (4.98)	−0.13	+0.02
Co(bztfo)$_3$ (**9**)	2.680 (4.19)	2.850 (4.31)	3.425 (4.85)		+0.25	+0.56
Co(bzpmo)$_3$ (**10**)	2.760 (3.90)		3.560 (4.64)	3.875 (4.70)	−0.27	−0.19
Co(hfac)$_3$ (**11**)	2.840 (3.82)	3.345 (4.18)		4.015 (4.61)	+0.50	+1.10
Co(dpmo)$_3$ (**12**)	3.170 (3.80)	3.320 (4.15)		3.790 (4.66)	−0.40	−0.40
Co(3-NO$_2$-acac)$_3$ (**13**)	3.075 [b]	3.485 (4.39)		3.845 (4.53)	+0.03	+0.37
Co(3-SCN-acac)$_3$ (**14**)	3.065 [b]	3.390 (4.23)		3.875 (4.50)	−0.03	(+0.62) [c]
Co(2-NO$_2$-bpdo)$_3$ (**15**)	2.910 (3.85)	3.420 (4.35)		3.840 (4.50)	−0.18	+0.51
Co(2-SCN-bpdo)$_3$ (**16**)	2.940 (3.84)	3.355 (4.30)		3.860 (4.51)	−0.20	(+0.62) [c]

[a] log (ϵ/mol^{-1} dm^3 cm^{-1}) in parentheses. [b] Unresolved bands. [c] Proposed value σ_m for the thiocyano group.

notable differences in the present series. Thus, the reduction of *B* and *C* proceeds in the same manner whereas in the case of the corresponding chromium(III) and iron(III) chelates the reduction of *B* is least in ligands where *C* is reduced most. In addition, the percentage change of *B* and *C* within the cobalt(III) series is as high as 65% and 28%, respectively. Furthermore, the nephelauxetic effect as evidenced by the reduction of *B* in terms of the substituent groups, R_1 and R_3, on the chelate rings follows the order: *t*-Bu, *t*-Bu > *t*-Bu, CH_3 > *t*-Bu, H > *t*-Bu, C_6H_5 > CH_3, C_6H_5 > CH_3, H > CH_3, CH_3 > H, C_6H_5 > C_6H_5, C_6H_5 > C_6H_5, CF_3 > CH_3, CF_3 > CF_3, CF_3. When the substituent R_2 is taken into account, both groups, $-NO_2$ and −SCN, should be placed before the hydrogen atom at the beginning of the series.

The portion of the electronic spectra resulting from transitions with energies higher than 2.4 μm^{-1} is more complicated because of the possibility of charge transfer and π–π^* transitions. The two bands appearing at about 2.7 and 3.2 μm^{-1} in the spectrum of tris(1,3-diphenyl-1,3-propanedionato)cobalt(III) (Co(dbm)$_3$) are considered as involving such CT transitions.[9,40]

Interestingly enough the position (Table V) and shape (Figure 2) of the low-energy band depend on the substituents and in certain cases, such as the chelates Co(bdo)$_3$, Co(bpdo)$_3$, and Co(bztfo)$_3$, it becomes a shoulder in the more intense high-energy band. The transitions observed are given in Table V. In the same table are listed the polarographic half-wave reduction potentials for the sufficiently reversible reaction Co(III)/Co(II) determined in acetonitrile solution. Details are given elsewhere.[19]

Discussion

Infrared Aspects. The influence of substituents attached to the carbonyl carbon atoms on the C=O and C=C frequencies of β-diketonato complexes has been discussed qualitatively by Nakamoto et al.[11] The evidence provided in the present study indicates that the shifts observed may be accounted for in terms of Hammett σ functions. The correlation of the carbonyl frequency with σ_p constants of adjacent substituents provides further information on the nature of the electronic interactions engendered by the substituents. It is known that the polarity of the bond is the main factor determining the infrared frequency of isolated vibrations such as the carbonyl stretching mode. The change in polarity of the $C\overset{\cdots}{-}O$ bond apparently results from change in electron density of the carbonyl carbon effected by the substituents, the change in charge density being then inductively transmitted to the carbonyl oxygen. Since the carbonyl band remains unsplit whenever only one substituent is present, resonance interaction with the oxygen atom in a para position relative to the substituent is envisaged as occurring through the "quasi-aromatic" ring.

Figure 1 shows that a good linear correlation of $\tilde{\nu}(C\overset{\cdots}{-}O)$ and $\sum\sigma_p$ is observed. Correlations with σ^+ and σ^- (not shown) are significantly poorer. This suggests that there is a restricted resonance enhancement of the $C\overset{\cdots}{-}O$ bond by delocalization of the charge from the cobalt(III) ion into the "quasi-aromatic" ring and the influence of the substituent is essentially inductive. These arguments are supported by the observed shifts in the C=C stretching vibrations, which may be interpreted accordingly. The inductive effect of the $-CF_3$ group should weaken the Co–O σ bonding, and this is confirmed by the lowering in the force constant in the corresponding chelates which can be inferred from the data in Table II.

Electronic Structure and Transitions. In the ligand field spectra of the tris(1,3-dionato)cobalt(III) complexes both spin-forbidden and spin-allowed $e_g \leftarrow t_{2g}$ transitions are observed. The low-energy bands are attributed to $^3T_{1g} \leftarrow {}^1A_{1g}$ and $^3T_{2g} \leftarrow {}^1A_{1g}$ transitions whereas the first spin-allowed band is assigned to the $^1T_{1g} \leftarrow {}^1A_{1g}$ transition. A fourth band, less well-resolved, is assigned to the $^1T_{2g} \leftarrow {}^1A_{1g}$ transition. The energies of these transitions are dependent on 10*Dq*, *B*, and *C*. The functional relationships including configuration interaction with higher energy states of the same symmetry were given by Tanabe and Sugano (eq 1–4). The number of bands observed is adequate to calculate a self-consistent set of parameters that one may rely upon. Indeed, insertion of the parameters thus obtained in eq 1–3 reproduces the observed energies adequately.

10*Dq*, which is effectively a measure of the difference in metal–ligand mixing between the frontier orbitals, the π-bonding t_{2g} set (HOMO) and the σ-antibonding e_g set (LUMO), varies very little in the present series. This contrasts with the substantial changes that occur in the other ligand field parameters (Table IV). Apparently the effect of overlap of the cobalt t_{2g} orbitals with the ligand π^* orbitals of proper symmetry and energy can be invoked to explain the delocalization of the d electrons. The extent of delocalization is influenced by the nature of the substituents within the β-dionato moiety. Electron-attracting groups, e.g. $-CF_3$, remove electron density from a cobalt–oxygen molecular orbital, thereby decreasing interelectronic repulsions. The delocalization is greater than that in the corresponding chromium(III) complexes.[38] This is expected for cobalt(III) since there is an increased tendency to covalency on moving toward the end of a given transition series.

Charge transfer has been invoked[9] for the appearance of the band (or shoulder) at about 2.7 μm^{-1}. There is some controversy about the direction of electron flow upon excitation,[9,32,40] and therefore, the assignment of the first CT band merits a few comments.

Barnum assigned the low-energy CT band in trivalent transition-metal acetylacetonates to a MLCT excitation since the energy of this transition increases as the central ion becomes more difficult to oxidize. Replacement of a methyl group adjacent to the carbonyl carbon atom by the $-CF_3$ group in β-diketones, as in trifluoroacetylacetone, Htfac, reduces the energy of the π^* levels

---

[40] Reed, J. L. *Inorg. Chem.* **1982**, *21*, 2829.

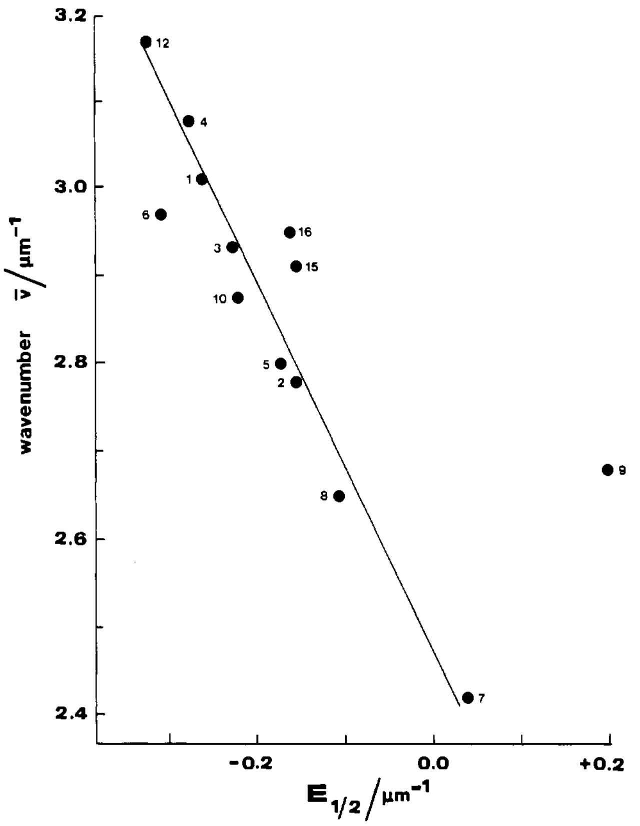


Figure 3. Correlation between the $E_{1/2}$ value and the wavenumber of the first charge-transfer transition.

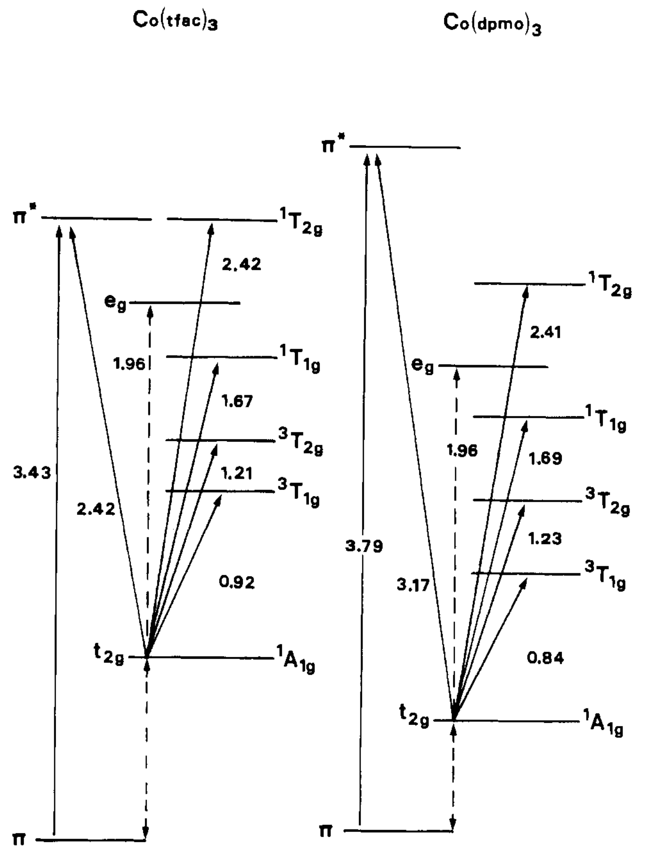


Figure 4. Diagram depicting the spacing of the LF excited states and the relative energies (in μm^{-1}) of the orbitals involved in the LF and CT transitions of the complexes Co(tfac)$_3$ and Co(dpmo)$_3$.

as a result of the inductive effect engendered by this group.[41] Therefore, the MLCT band in Co(tfac)$_3$ should occur at longer wavelengths than in Co(acac)$_3$ as in fact is observed (Table V). This implies that the MLCT optical electronegativity of tfac$^-$, χ_{opt}(tfac$^-$), will be greater than that of acac$^-$. Inserting the spectroscopically determined parameters into Jørgensen's relationship,[37] one obtains $\chi_{opt}(\text{acac}^-) = 1.20$ and $\chi_{opt}(\text{tfac}^-) = 1.42$. Although it is true that there is no suitable reference with which to compare these values, they seem acceptable for unoccupied π-antibonding ligand molecular orbitals.[42] The apparent sensitivity of the χ_{opt}(L) values to substitution and the dependence of the changes on the electronic effects induced by the substituents corroborate the proposed assignment. Since the polarographic reduction potentials, $E_{1/2}$, of this series are linearly dependent on Hammett σ parameters,[19] the MLCT transition energies should correlate with $E_{1/2}$, as actually happens (Figure 3). Figure 3 indicates that the charge-transfer spectral behavior of Co(hfac)$_3$ and Co(bztfo)$_3$ deviates markedly from the trend exhibited by the other chelates of this series although their electrochemical behavior follows the same pattern. Since the electrochemical electron acquisition is related to the LUMO e$_g$ orbitals whereas the MLCT transition involves the ligand π^* orbitals, the explanation for the anomalous behavior of Co(hfac)$_3$ and Co(bztfo)$_3$ should be sought in the influence of the substituents on the ligand antibonding orbitals. Attachment of a strong electron-accepting group, e.g. CF$_3$, to one carbonyl carbon atom reduces the energy of the $\pi^* \leftarrow \pi$ transition whereas the simultaneous presence of such groups on both carbonyl carbon atoms increases the energy requirements for a $\pi^* \leftarrow \pi$ transition. Indeed, the $\pi^* \leftarrow \pi$ transition in Hacac is observed[41] at 3.57 μm^{-1} while the same transition in Htfac occurs at 3.52 μm^{-1}. Insertion of another $-$CF$_3$ group as in Hhfac increases the energy requirements appreciably so that the $\pi^* \leftarrow \pi$ transition occurs at 3.66 μm^{-1}. The information obtained spectroscopically may be used in conjunction with the electrochemical data to construct a naive one-electron molecular orbital scheme for the representation of the observed transitions. A suitable point of reference appears to be the energy of the e$_g$ orbitals (LUMO) since (1) these orbitals are involved in the electronic transitions, (2) the electron acquired in the electrochemical reductions is transferred to these orbitals, and (3) there is fair estimation of their energy from quantum-mechanical calculations. Sock and co-workers[43] have found that the absolute reduction potentials of several M(acac)$_3$ chelates are in concordance with the theoretically calculated energies of the acceptor orbitals of these compounds.[32] The polarographic half-wave potentials of this series of cobalt(III) chelates (Table V) should be corrected[44] since the actual value of the reference electrode (SCE) is $E^\circ_{SCE} = -5.06$ eV. Therefore, the energy of the LUMO e$_g$ orbitals corresponds to the sum $E_{1/2} + E^\circ_{SCE}$ and for Co(acac)$_3$ this comes out to be -5.40 eV, which is equivalent to -4.350 μm^{-1}, the value obtained by Barnum[32] using Hückel LCAO–MO calculations. The energy of the filled t$_{2g}$ orbitals (HOMO) may then be obtained since the parameter 10Dq has been determined spectroscopically.

For comparison purposes it is useful to give diagrammatically the spectroscopic data of two complexes, such as Co(tfac)$_3$ and Co(dpmo)$_3$, with appreciably different reduction potentials and charge-transfer excitation energies. Figure 4 depicts the relative energies of the orbitals involved in the assignment of the spectral bands of the two complexes Co(tfac)$_3$ and Co(dpmo)$_3$ and illustrates the spacing of the excited states arising from electronic transitions within the metal-localized orbitals. From these diagrams the effect of the substituents $-$CF$_3$ and $-$C(CH$_3$)$_3$ on the energy of the ligand π^* orbitals becomes apparent and, consequently, the reason for the observed differences in the wavenumber

---

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

(42) Byers, W.; Fa-Chun Chou, B.; Lever, A. B. P.; Parish, R. V. *J. Am. Chem. Soc.* **1969**, *91*, 1329.

(43) Sock, O.; Lemoine, P.; Gross, M. *Electrochim. Acta* **1981**, *26*, 99.

(44) Stanieda, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1968**, *23B*, 1285.

of the charge-transfer excitation and in the reduction potential for this series of cobalt(III) chelates. The proximity of the $^1T_{2g}$ and CT excited states explains why the $^1T_{2g} \leftarrow {}^1A_{1g}$ transition is difficult to observe.

Registry No. *fac*-**1**, 60733-43-9; *mer*-**1**, 60684-52-8; *fac*-**2**, 41765-60-0; *mer*-**2**, 41768-47-2; *fac*-**3**, 105617-40-1; *mer*-**3**, 105617-42-3; **4**, 21679-46-9; *fac*-**5**, 41768-44-9; *mer*-**5**, 41768-43-8; *fac*-**6**, 23331-43-3; *mer*-**6**, 23302-00-3; *fac*-**7**, 41768-44-9; *mer*-**7**, 41768-43-8; **8**, 21679-34-5; **9**, 31125-84-5; *fac*-**10**, 105617-45-6; *mer*-**10**, 105617-41-2; **11**, 16702-37-7; **12**, 14877-41-9; **13**, 15169-25-2; **14**, 16702-37-7; *fac*-**15**, 105563-50-6; *mer*-**15**, 105617-43-4; *fac*-**16**, 105563-51-7; *mer*-**16**, 105617-44-5.

Contribution from the Department of Chemistry,
McGill University, Montreal, Quebec, Canada H3A 2K6

Spin–Lattice Relaxation Time Studies and Vibrational Spectra of Solid Tricarbonyl(η^7-tropylium)chromium(0) and -molybdenum(0) Tetrafluoroborates, [(η^7-C_7H_7)M(CO)$_3$]BF_4 (M = Cr, Mo)

Pierre D. Harvey, Ian S. Butler,* and Denis F. R. Gilson*

Received April 25, 1986

The proton and ^{19}F spin–spin lattice relaxation times (T_1) of the solid, group VIB (6^{46}) tricarbonyl(η^7-tropylium)metal(0) tetrafluoroborates, [(η^7-C_7H_7)M(CO)$_3$]BF_4 (M = Cr, Mo), have been measured over the 296–93 K temperature range. The activation energies (kJ mol^{-1}) for arene ring rotation in the two complexes are quite similar: Cr, 12.8; Mo, 13.6. X-ray powder diffraction patterns of the Cr, Mo, and W complexes at room temperature indicate that the three complexes are isostructural. The activation energies (kJ mol^{-1}) for BF_4^- reorientation are different: Cr, 6.77; Mo, 12.3. Nonbonded atom–atom potential calculations show that the barriers to tropylium ring rotations are due to ring–carbonyl and ring–BF_4^- interactions in about equal amounts. Similar calculations on BF_4^- reorientation indicate that rotations around the 3-fold axes have lower barriers than do rotations about the 2-fold axes. The FT-IR and Raman spectra of the Cr and Mo complexes have also been investigated at room and low temperature, and some vibrational assignments are proposed. The spectroscopic results, together with differential scanning calorimetry data, confirm the absence of any phase changes for the complexes in the 296–80 K temperature range.

Introduction

The possible bonding modes and conformations of the aromatic rings in π-arene organometallic complexes of the type (η^n-C_nH_n)M(CO)$_3$ (M = transition metal; n = 4–7) have been the subject to renewed interest of late.[1-3] It is now clear that the arene rings do not possess the ideal symmetries expected for a regular square, pentagon, hexagon, etc.[4-15] In addition, very low barriers to ring rotation are predicted for (η^4-C_4H_4)-, (η^5-C_5H_5)- and (η^7-C_7H_7)ML_3 complexes.[3] For a clearer understanding of the motional behavior of the π-arene compounds, it is important to have information on the dynamics, as well as the structures of the complexes, in order to obtain realistic estimates of the potential barriers to arene group rotation in the solids.

Over the past 5 years, there have been several investigations of the barriers to π-arene ring rotation in solid organometallic complexes, e.g. the cyclobutadienyl ring in (η^4-C_4H_4)Fe(CO)$_3$[16] and the cyclopentadienyl ring in various derivatives such as (η^5-C_5H_5)Mn(CO)$_3$.[17-19] The principal approaches have been to study the temperature dependence of the proton spin–lattice relaxation times and to perform nonbonded atom–atom potential calculations. The calculations have provided useful information on the origin and magnitude of the various contributions to the rotational barriers,[19,20] which are directly dependent on the packing and the sites occupied by the molecules in the unit cell. Chhor and Lucazeau[21-23] have used vibrational spectroscopy and neutron-scattering techniques to estimate the barrier heights to ring rotation in several solid organometallic systems.

A natural extension of the earlier work on π-arene ring systems in organometallic complexes would be to the 7-membered tropylium ring (C_7H_7) in such complexes as TrV(CO)$_3$ and [TrM(CO)$_3$]BF_4 (Tr = η^7-C_7H_7; M = Cr, Mo, W). The vanadium complex is not suitable for NMR studies because of its paramagnetism.[24] The crystal structure of the molybdenum salt has been published, and it appears that it was difficult to locate the

---

(1) Chinn, J. W., Jr.; Hall, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 4930.
(2) Chinn, J. W., Jr.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 2759.
(3) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149.
(4) Day, V. W.; Reimer, K. J.; Shaver, A. *J. Chem. Soc., Chem. Commun.* **1975**, 404.
(5) Mitschler, A.; Rees, B.; Lehmann, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 3390.
(6) Day, V. W.; Stults, B. R.; Reimer, K. J.; Shaver, A. *J. Am. Chem. Soc.* **1974**, *96*, 1227.
(7) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 277 and references therein.
(8) Fitzpatrick, P. J.; Lepage, Y.; Sedman, J.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2852.
(9) Fitzpatrick, P. J.; Lepage, Y.; Butler, I. S. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *37*, 1052.
(10) Yannoni, C. S.; Caeser, C. P.; Dailey, B. P. *J. Am. Chem. Soc.* **1967**, *89*, 2833.
(11) Bailey, D.; Buckingham, A. D.; Rest, A. J. *Mol. Phys.* **1973**, *26*, 233.
(12) Emsley, J. W.; Lindon, J. C. *Mol. Phys.* **1974**, *28*, 1373.
(13) Diehl, P.; Moia, F.; Boesiger, H.; Wirz, J. *J. Mol. Struct.* **1983**, *98*, 297.
(14) Gilson, D. F. R. *J. Mol. Struct.* **1985**, *127*, 121.
(15) Gilson, D. F. R.; Fitzpatrick, P. J.; Butler, I. S. *Organometallics* **1984**, *3*, 387.
(16) Harvey, P. D.; Butler, I. S.; Gilson, D. F. R. *Inorg. Chem.* **1986**, *25*, 1009.
(17) Butler, I. S.; Fitzpatrick, P. J.; Gilson, D. F. R.; Gomez, G.; Shaver, A. *Mol. Cryst. Liq. Cryst.* **1981**, *71*, 213.
(18) Gilson, D. F. R.; Gomez, G.; Butler, I. S.; Fitzpatrick, P. J. *Can. J. Chem.* **1983**, *61*, 737.
(19) Gilson, D. F. R.; Gomez, G. *J. Organomet. Chem.* **1982**, *124*, 41.
(20) Cambell, A. J.; Fyfe, C. A.; Harold-Smith, D.; Jeffrey, K. R. *Mol. Cryst. Liq. Cryst.* **1976**, *36*, 1.
(21) Chhor, K.; Lucazeau, G. *Inorg. Chem.* **1984**, *23*, 462.
(22) Lucazeau, G.; Chhor, K.; Pommier, C. *Spectrosc.: Int. J.* **1983**, *2*, 79.
(23) Chhor, K.; Lucazeau, G. *J. Raman Spectrosc.* **1982**, *13*, 235.
(24) Allegra, G.; Perego, G. *Ric. Sci., Parte 2: Ser. A* **1961**, *1*, 362.

0020-1669/87/1326-0032$01.50/0