Figure 9. Relationship between $\nu(\text{RuO}) - \nu(\text{RuRu})$ and $I(\nu_2)/I(\nu_1)$ for the carboxylate complexes of the type $\text{Ru}_2(\text{O}_2\text{CR})_4\text{Cl}$ (R = CH$_3$, C$_2$H$_5$, or C$_3$H$_7$) at 514.5-nm excitation.

in all cases. The explanation of this unexpected observation may lie in the fact that $\nu(\text{RuRu})$ and $\nu(\text{RuO})$ are closest in wavenumber in the case of the acetate and, therefore, that the RuRu and RuO symmetry coordinates are coupled most

strongly in this case. This would, of course, lead to the greatest intensity borrowing for ν_2 and associated modes of the acetate complex, a situation made clear in Figure 9 for the various complexes of the sort $\text{Ru}_2(\text{O}_2\text{CR})_4\text{Cl}$; note especially that for the ^{18}O-substituted acetate complex, $I(\nu_2)/I(\nu_1)$ is much higher than that for the unsubstituted complex, a particularly compelling result in this context.

Although the observation of combination-band progressions of the sort $v_1\nu_1 + v_2\nu_2$ is not, of itself, a consequence of the Duschinsky effect (the change in composition of the Q_1 and Q_2 normal coordinates, in terms of their constituent symmetry coordinates, on electronic excitation),[25–27] the possibility that the change, with v_1, of the relative intensities of members of the $v_1\nu_1$ and $\nu_2 + v_1\nu_1$ progressions is so (Figure 1), requires further consideration.

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The Problem of π-Electron Delocalization in Group 4 Acetylacetonate Complexes, M(acac)₂X₂, As Studied from the Optical Spectra

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Absorption and reflectance spectra of *cis*-dihalobis(2,4-pentanedionato) complexes of Ti(IV), Zr(IV), Ge(IV), and Sn(IV) have been measured under water- and alcohol-free conditions. The majority of absorption maxima in the vis–UV region is assigned to π–π* transitions of the acetylacetonate ligands which are subject to the effect of different degrees of metal–ligand π-electron bonding. Significant π bonding, as realized in the titanium compounds, leads to electron delocalization over the complex molecule and increases the splitting of the various π–π* band components. Ligand to metal charge-transfer transitions are likely only for the iodo complexes. However, π-bonded acetylacetonate intermixes ligand–metal charge-transfer states into π,π* excited states which is particularly effective in Ti(IV) complexes. Halogen ligands are able to perturb this mechanism more effectively when π-electron delocalization is large. The intermixing of charge-transfer states is important for relatively large metal optical electronegativities which are a measure of the availability of these energy levels.

Introduction

β-Diketones can bind in a variety of ways to metallic ions.[1] In the most common species the diketone is present as an enolate anion acting as a bidentate ligand via the oxygen atoms. Optical spectra in absorption and emission have been measured frequently although in many cases the bands could not be assigned with confidence, since comparison with theoretical results could not be made, due to the lack of reliable calculations. Because of its metal–ligand π-bonding capability,[2] questions concerning the ring current[3] (aromaticity) in the chelate are raised, and the problem of delocalization of ligand π-electrons over the whole complex is pertinent.

Early theoretical work[4,5] starts with assumption of delocalized electrons, by applying convenient Hückel MO theory. However, a closer analysis of spectra, performed with a theoretical procedure of higher sophistication which uses a localized model, results in a better understanding of experimental findings on closed-shell as well as open-shell metal tris(acetylacetonates).[6] The application of the latter model is also easy for the very simple spectrum of closed-shell complex compounds, which is characteristic of many acetylacetonates. The result agrees well with the assignment obtained from the CD spectrum of the complex ion[7] [Si(acac)₃]⁺ which allows

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the absorption spectrum to be explained by $\pi-\pi^*$ transitions within each of the ligands which in the complex are perturbed by electron repulsion on different ligands, leading for D_3 symmetry to an assignment of $A_1 \rightarrow A_2$ for the main band and to $A_1 \rightarrow E$ for the shoulder on the long-wavelength side. A quite similar CD spectrum has been obtained for [Ge-(acac)₃]⁺.[8] In view of these findings, any attempts to interpret one of these absorptions as being due to n–π^* transitions in the ligands[9,10] or to charge transfer from acetylacetonate to the metal[11] are of only minor importance. If these mechanisms were operative in this spectral region, they could contribute only small portions to the oscillator strengths of these absorptions. Yet these possibilities should not be excluded in discussion of acetylacetonate spectra.

When a definite π bonding exists between the central metal and the ligands, the π orbitals extend over the whole molecule and are classified according to representations of the molecular point group. In a tris complex of D_3 symmetry, five electric dipole-allowed transitions from the ground state are possible.[12] Unless certain accidental or near degeneracies occur, the model for delocalized π bonds is not able to explain the observed spectra for tris(acetylacetonate) complexes. This has been demonstrated with the localized model by considering additional terms in the wave functions to include delocalized states.[6]

A systematic investigation of the problem of π-electron delocalization by means of optical spectra should begin with closed-shell complexes in order to avoid complication with other electron transition mechanisms (d–d and d–π^*). Until now, there has been little experimental evidence for compounds in which metal–ligand π bonding is significantly large. The increased downfield chemical shift of the proton magnetic resonance[3] in [Ti(acac)₃]⁺ and the small O–O "bite" of the chelating ligand in [Ti(acac)₃](ClO₄),[13] [Cl₃Ti(acac)]₂,[14] and [Ti(acac)₂(2,6-diisopropylphenoxo)₂],[15] which is considerably shorter than that found in other acetylacetonate systems,[16] suggest an increased effective nuclear charge at titanium and support a significant p_π–d_π bonding due to an improved orbital overlap. In this context it should be noted that also the ultraviolet spectrum of [Ti(acac)₃](ClO₄) in CH₃CN differs from spectra of similar systems.[17]

In order to clarify these questions by spectroscopic means, we examine a series of group 4 acetylacetonates of the type cis-[M(acac)₂X₂] (X = halogen) in the present paper. The central metal ions studied were Sn⁴⁺ and Ge⁴⁺, which are considered to be weakly π bonding, and Ti⁴⁺ and Zr⁴⁺, for which enhanced π bonding has been suggested.[14,15] The spectra of homologous compounds can be compared by varying the halogen ligands, illustrating the change in the electronic structure of the central metal. This group of compounds has also been investigated by proton magnetic resonance,[19] from which larger π bonding has been suggested for all pretransition elements, i.e., for Ti⁴⁺, Zr⁴⁺, and Hf⁴⁺. Ultraviolet spectra of Ti⁴⁺ and Zr⁴⁺ compounds have been previously reported in a thesis, in which some preliminary assignments are also discussed.[18]

Experimental Section

(a) Reagents. Germanium tetrachloride (EGA-Chemie 99%), tin tetrahalogenides (F, Ferak 99%; Cl, Merck; Br, Merck), titanium tetrahalogenides (all Ferak 98–99%), zirconium tetrachloride (Merck-Schuchardt 99%), and copper(II) acetylacetonate (Merck-Schuchardt 98%) were used as purchased without further purification. Tin tetraiodide was prepared from tin and iodine. Acetylacetone was distilled immediately before use. Those organic solvents which were not reagent grade were purified by distillation. Chloroform, dichloromethane, and ethyl acetate were dried with use of molecular sieves (4 Å, Merck). Diethyl ether, benzene, and hexane were refluxed over sodium–lead alloy, to remove the bulk of moisture, and subsequently over lithium aluminum hydride under dry-nitrogen atmosphere and later distilled.

(b) General Techniques. Since M(acac)₂X₂ complexes are readily hydrolyzed in solution (increasing in the order Ge < Sn < Ti < Zr), synthesis and all subsequent handling of the compounds were carried out under anhydrous conditions, keeping the material in a closed system under a dry-nitrogen atmosphere. The glassware was dried at 150 °C, and all equipment was twice evacuated and rinsed with dry nitrogen. When new connections were made, the system was kept under a slight nitrogen overpressure. Products were filtered over a glass frit in a tube with a side-arm nitrogen inlet and a stopcock below the frit. Recrystallizations were carried out in a two-necked flask under dry nitrogen. The complexes were dried in vacuo and stored in a glovebox under dry nitrogen.

(c) Complexes. The following compounds were prepared as described in the literature: Ge(acac)₂Cl₂,[20] Sn(acac)₂X₂ (X = F, Cl, Br, I),[21–23] Ti(acac)₂X₂ (X = F, Cl, Br),[24,25] and Zr(acac)₂Cl₂.[26,27] However, some changes were found to be useful: for Sn(acac)₂Br₂ the reaction time was increased to 3 h, Zr(acac)₂Cl₂ was recrystallized from benzene, and solutions of Sn(acac)₂I₂ were protected from exposure to light. The identity and purity of the materials were controlled by elementary analysis, by measuring melting points (with use of a Büchi SMP 20 apparatus), infrared spectra (Perkin-Elmer 325 grating spectrophotometer), and ¹H NMR spectra (Hitachi Perkin-Elmer R-24B spectrometer). The results agree well with published data,[19–22,24,28,29] except for Zr(acac)₂Cl₂, which decomposed at 189–193 °C, in contrast to various data reported in the literature, e.g., 180.5–182[26,27] and 233–235 °C.[30]

(d) Absorption Spectra. Optical spectra were recorded with use of a Varian Cary 17 spectrophotometer. Criteria governing the choice of appropriate solvents for recording spectra were, in particular, transparence in the spectral region and indifference to reactions or specific interactions (solvent effects ought to be excluded as far as possible). The solvents chloroform, dichloromethane, and cyclohexane have met these demands satisfactorily; on the other hand alcohols alter the absorption spectra of complexes which are also water sensitive within a short period of time. Great care had to be taken to prevent hydrolysis in all solvents used. The solvents were dried and freed from alcohols by LiAlH₄. They were stored under dry nitrogen and used for preparing solutions in a glovebag (I²R polyethylene glovebag). The Suprasil quartz cells were closed by Teflon stoppers. Each measurement was repeated several times, including immediately following the first spectrum, in order to check on possible hydrolysis. With the water content in the purified solvents estimated to be of the order of 10⁻⁴ M, the concentration still would be large enough to react in a short period of time with the most sensitive compound, Zr-(acac)₂Cl₂. The action of hydrolysis was examined by following the spectral change of CH₂Cl₂ solutions with a small amount of water added.

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Table I. Absorption Maxima (×10³ cm⁻¹) of M(acac)₂X₂ in Various Solvents at Room Temperature

M	X = F			X = Cl			X = Br			X = I		
	CHCl₃	CH₂Cl₂	C₆H₁₂	CHCl₃	CH₂Cl₂	C₆H₁₂	CHCl₃	CH₂Cl₂	C₆H₁₂	CHCl₃	CH₂Cl₂	C₆H₁₂
Ge				34.7 sh^a	34.7 sh	c						
				33.6 (2.0)^b	33.6 (2.0)							
				31.8 sh	31.8 sh							
				31.3 sh	31.3 sh							
Sn									43.5 sh			43.5 sh
	34.1 (2.5)	34.1 (2.6)		33.4 (2.7)	33.5 (2.7)	33.5 (2)	33.1 (2.7)	33.2 (2.7)	33.2 (2.2)	32.7 (2.7)	32.7 (2.6)	32.7 (2.3)
	32.8 sh	32.9 sh		32.5 sh	32.6 sh	32.6 sh	32.2 sh	32.2 sh	32.3 sh	31.7 sh	31.7 sh	31.7 sh
Ti			46.5 sh			45.5 sh			44.4 sh			
	39.7 (1.4)	39.8 (1.4)	40.1	37.9 (1.7)	37.9 (1.7)	37.9	37.3 (1.4)	37.4 (1.4)	37.3			
	29.1 (0.7)	29.1 (0.7)	29.4	26.8 (0.5)	26.9 (0.5)	27.5	29.9 (0.7)	30.1 (0.8)	29.9			
							27.0 sh	27.0 sh	27.0 sh			
Zr				36.3^d (0.5)	36.4^d (0.6)	36.6^d						
				30.9 (1.2)	30.9 (1.1)	31.0						

^{a} Positions of band shoulders are estimated. ^{b} Extinction coefficients (×10⁻⁴) in brackets are given in L mol⁻¹ cm⁻¹. ^{c} Not solvable. ^{d} Uncertain (see text).

Table II. Reflectance Spectra at 80 K of M(acac)₂X₂

	F	Cl	Br	I
Ge		39.2 sh (0.66)^a		
		33.9 (1)		
		31.3 sh (0.55)		
Sn	39.2^b	38.9 sh (0.44)	38.6 sh (0.57)	37.7 sh (0.75)
	33.7 (1)	33.2 (1)	33.1 (1)	32.7 (1)
	31.5 sh (0.59)	31.4 sh (0.55)	31.1 sh (0.52)	29.4 sh (0.50)
Ti	39.5 (1)	38.6 (1)	37.9 (1)	
	35.2 sh (0.85)	30.9 sh (0.86)	29.0 sh (0.91)	
	30.0 (0.75)	28.0 (0.87)	25.0 (0.93)	
	25.1 sh (0.50)	24.9 sh (0.81)	17.9 (0.65)	
Zr		38.5 sh (0.64)		
		31.6 (1)		
		29.2 sh (0.79)		

^{a} Relative intensity. ^{b} Inflection.

(e) Reflectance Spectra. Measurements in the region 650–245 nm were carried out on a Varian Cary 17 spectrophotometer equipped with a Cary Model 1711 diffuse reflectance accessory. The samples were powdered and diluted with barium sulfate (Spectrograde, dried at 150 °C) in a glovebox under dry-nitrogen atmosphere and transferred to a flow cryostat (Oxford Instruments CF 100). The reflectance spectra were recorded at room temperature and at liquid-nitrogen temperature with pure barium sulfate as a standard. The temperature was followed by a thermocouple attached to the sample mount. The reflectance spectra were reproducible for each sample; however, different preparations resulted in slightly different spectral curves due to variations in the grain size, surface properties, etc.

(f) Computer Programming. Band analyses have been carried out in terms of Gaussian band profiles. In all cases the spectra are simulated with a least-squares fit by independent variation of band parameters (band maxima, intensities, and half-width) for a minimal number of bands. The largest error obtained from the formula $[\sum_i^N (x_i^{exptl} - x_i^{calcd})^2/N]^{1/2}$ ($x = 10^{-4}\epsilon$) was on the order of 0.01 and did not exceed 0.023. The parameters were used for calculating oscillator strengths.

Results and Discussion

In Table I the absorption spectra are listed with use of those solvents in which the complex compounds do not react during the recording time with minor impurities such as water and alcohol. Comparison with reflectance spectra (cf. Table II) permitted identification of possible reactions with solvent and illustration of solvent effects. The results indicate that absorption spectra of alcoholic solutions, as reported by Nelson,[31] and experiments performed in these solutions[22,32] cannot be reliable. The reaction of the complex compounds with alcohol is so rapid that only spectra of decomposition products are measured. The tin complexes yield a band at 36.4 × 10³ cm⁻¹
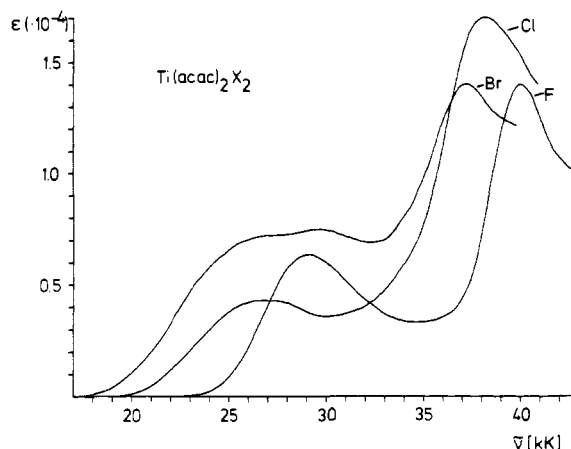
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Figure 1. Absorption spectra of Ti(acac)₂X₂ solutions in CH₂Cl₂ at room temperature.

($\epsilon = 1.7 \times 10^4$) with shoulders at ca. 32.8 and 34.5 × 10³ cm⁻¹ which seems to indicate, among other decomposition products, the formation of free acetylacetone molecules. Deterioration of spectra of solutions in carefully dried CHCl₃, CH₂Cl₂, and C₆H₁₂ was observed after a few minutes only for the titanium and zirconium compounds. Addition of small amounts of water altered all spectra within the usual recording time. Therefore, it can be concluded that, with the solvents of Table I, reliable spectra of the complex compounds were obtained with a relatively small solvent effect. This is supported by the results obtained by reflectance measurements.

At first glance the tables show that the spectra of the titanium compounds are markedly different from those of the other compounds. While most of the spectra have only one strong band with a shoulder on the long-wavelength side, which is characteristic for almost all closed-shell acetylacetonates,[6,9] in the titanium compounds two separate absorption bands can be detected which are at least 10 × 10³ cm⁻¹ apart. From the reflectance spectra it is evident that more than two transitions must be present. In Figure 1 the absorption spectra of the titanium complexes are illustrated. For comparison the other type of spectrum is given in Figure 2, which shows the absorption curve of Ge(acac)₂Cl₂ in which a higher resolution was obtained than for other compounds.

Larger band shifts were observed only in the titanium series of compounds. Since no larger shifts were observed for the tin homologues it can be concluded that the main bands are not due to an electron transfer from the halogens to empty central metal orbitals. Such charge-transfer transitions can be predicted by applying the concept of optical electronegativity,[33] according to which spin-allowed transitions within the
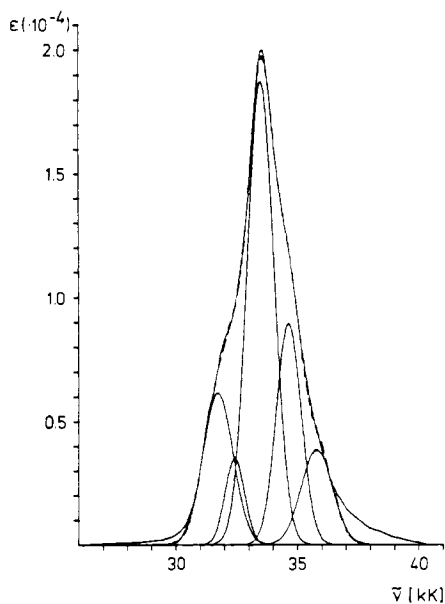
Figure 2. Absorption spectrum of Ge(acac)₂Cl₂ dissolved in CH₂Cl₂ and band analysis by gaussian curves. The dashed line indicates the curve obtained from superposition.

Figure 3. Gaussian curve analysis of the Ti(acac)₂Br₂ absorption spectrum.

Figure 4. Band analysis of the Sn(acac)₂F₂ spectrum obtained from (a) four and (b) two primitive gaussian curves.

relevant spectral region are expected for Sn(acac)₂Br₂ at 39 × 10³ cm⁻¹, Sn(acac)₂I₂ at 30 × 10³ cm⁻¹, Ti(acac)₂Cl₂ at 28.5 × 10³ cm⁻¹, and Ti(acac)₂Br₂ at 22.5 × 10³ cm⁻¹. Also charge transfer of π electrons from the acetylacetonate ligands to the central metal should occur in this energy range if the optical electronegativity is near χ_{acac} = 2.7, as has been proposed from the spectra of tris(acetylacetonate) complexes of transition-group ions.[11]

For an explanation of the bands in this spectral region, the mechanism of internal π–π* transitions within the acetylacetonate ligands must first be considered. Free acetylacetone in CHCl₃ has a band at 36.5 × 10³ cm⁻¹, due to a $\pi_3 \rightarrow \pi_4$ orbital transition,[4,34] which is shifted in complex compounds by only (1–3) × 10³ cm⁻¹ to smaller wavenumbers.[9,34] As mentioned above, the π–π* transitions are split into several components, depending on the delocalization of π electrons and if the compound has more than one acetylacetonate ligand due to electron repulsion. Since the present compounds contain two of these ligands, more than one π–π* transition must be expected, which may be either localized at one ligand or delocalized over the molecule. Even though no charge-transfer transitions from the ligands to the metal could be identified in the near-UV spectrum, an intermixing of such states into the low-lying π-electron states must nevertheless be considered. In particular, the titanium complexes, which, judging from the optical electronegativity of Ti(IV), χ_{Ti} = 2.05, have relatively low-energy charge-transfer states, are candidates for significant intermixing of charge-transfer configurations into π-electron states. This intermixing can only be effective if metal–ligand π bonding is large enough, which promotes π-electron delocalization and therefore destroys the classification of bands into π–π* and charge-transfer transitions.

So that a more reliable assignment could be achieved, a band analysis was carried out by resolving the spectra into the smallest possible number of gaussians for a given error limit (see Experimental Section). Figure 3 shows for one case how closely such a simulation of the measured spectrum can fit the experimental curve. Figure 4 demonstrates that, for a satisfactory decomposition, the spectra of the tin complexes must
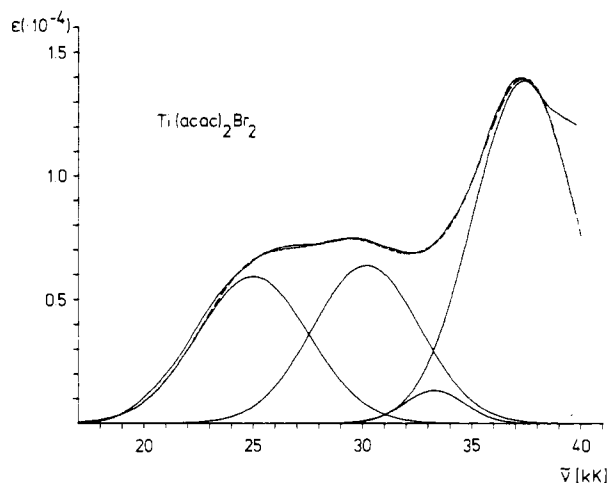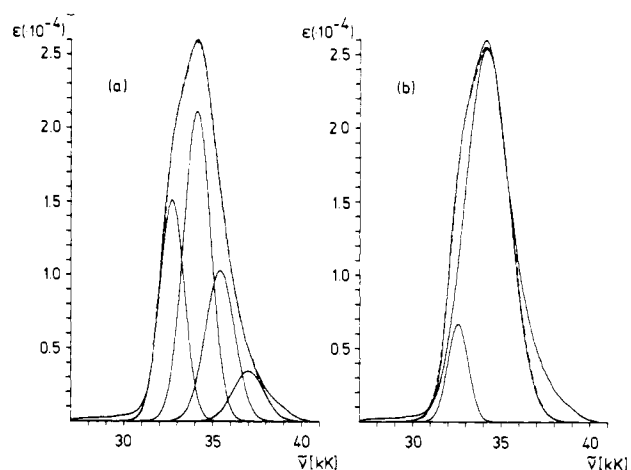
be resolved into four gaussians instead of two. The error calculated with use of the above formula for a four-gaussian adaptation of Sn(acac)₂F₂ was 0.013 and increased for a simulation with two gaussians to 0.11. The different half-widths of the two bands when the spectrum is approximated by two gaussians would lack physical reality, since both would represent π–π* transitions which are localized at each of the ligands, only slightly perturbed by electron repulsion. In Table III the results obtained from the band analyses are compiled, together with band splittings and relative values for oscillator strengths.

An interpretation of the spectra now proceeds as follows. If in titanium complexes ligand–metal π bonding is effective, as has been proposed from NMR results,[3,19] the delocalized π-bonding model[4,5] explains the four absorption bands in C_2 symmetry notation by transitions from a and b orbitals arising from free ligand π_3 orbitals to molecular orbitals of the same symmetry type, which result from linear combinations of π_4* orbitals. The overall splitting of (11–12) × 10³ cm⁻¹ did not depend very much on the halogen ligands. No band shifts characteristic of halogen–metal charge-transfer transitions within the homologues could be detected. However, an intermixing of halogen–metal charge-transfer states into the π states would increase in the series F, Cl, Br. As metal–halogen bonding interacts increasingly in this sequence with the π-electron system of the molecule, the total oscillator strength is changed to larger values. Similarly large differences in oscillator strengths were not observed for the tin series (cf. Table III). The assignment of the bands as due primarily to

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Table III. Results of Band Analyses of Absorption Spectra in CH_2Cl_2 and Oscillator Strengths of $M(acac)_2X_2$ Complexes

M	X	$10^3\bar{\nu}$, cm^{-1}	$10^3\delta$, cm^{-1}	f_i	Σf_i
Ge	Cl	31.7	1.5	0.04	0.25
		32.4	0.9	0.02	
		33.5	1.3	0.11	
		34.6	1.2	0.05	
		35.8	1.5	0.03	
Sn	F	32.7	1.6	0.11	0.40
		34.1	1.8	0.17	
		35.4	1.9	0.09	
		37.0	2.0	0.03	
Sn	Cl	32.2	1.5	0.11	0.42
		33.5	1.8	0.18	
		34.8	1.8	0.09	
		36.3	2.0	0.04	
Sn	Br	32.0	1.4	0.10	0.42
		33.2	1.8	0.18	
		34.4	1.8	0.08	
		35.8	2.3	0.06	
Sn	I	29.8	1.3	0.01	0.50
		31.4	1.6	0.11	
		32.7	1.8	0.17	
		34.1	1.8	0.12	
		35.7	2.0	0.09	
Ti	F	28.8	4.7	0.13	0.47
		33.2	5.1	0.07	
		35.8	2.3	0.01	
		40.0	4.0	0.26	
Ti	Cl	26.0	5.7	0.10	0.60
		31.2	5.8	0.08	
		33.6	2.9	0.02	
		38.1	5.1	0.40	
Ti	Br	25.0	6.0	0.16	0.71
		30.2	5.8	0.17	
		33.3	3.3	0.02	
		37.4	5.6	0.36	
Zr	Cl	30.7	3.2	0.16	
		33.1 (36.3)	3.1 (5.2)	0.04 (0.12)	

$\pi-\pi^*$ transitions is supported by the spectrum of [Ti(acac)$_3$](ClO$_4$),[17] which is closely similar to the Ti(acac)$_2$X$_2$ spectra: the tris(acetylacetonate) complex has bands at 27.5 × 10^3 (ϵ = 0.8 × 10^{-4}) and 38.9 × 10^3 cm^{-1} (2.2 × 10^{-4}), which are also about 11 × 10^3 cm^{-1} apart. Significant splittings of $\pi-\pi^*$ transitions due to π-electron bonding have also been found for transition-metal acetylacetonates.[4,5,12] As for any tris(acetylacetonates) of D_3 symmetry with ligand-metal π bonding, a maximum of five symmetry-allowed $\pi-\pi^*$ transitions must be expected in this region. For all titanium acetylacetonates an intermixing of excited electron configurations, belonging to a charge transfer from acetylacetonate ligands to the central metal, into excited π-electron states is significant. These charge-transfer contributions are, however, not predominant as it is indicated from spectral variations on changing halogen coordination (see below). The relatively large splitting of (11–12) × 10^3 cm^{-1} may be caused by this intermixing.

The series of tin compounds are representatives for metal-ligand π bonding of limited strength. A certain degree of π bonding must be present in order to explain the stability of the cis geometry, since in this case all three t_{2g} orbitals would be involved in the π-bonding system while in a sterically favored trans compound only two t_{2g} orbitals could form a metal-acac π bond.[35]

Only two transitions are expected if the π electrons are localized on the ligands and coulombic repulsion of electrons on different ligands removes the degeneracy of the $\pi_3 \rightarrow \pi_4^*$ transitions. The wave functions for the two excited states using C_2 symmetry notation are

$$\Psi(A) = (1/2)^{1/2}(\psi_a\psi_b' + \psi_a'\psi_b)$$
$$\Psi(B) = (1/2)^{1/2}(\psi_a\psi_b' - \psi_a'\psi_b)$$

where ψ_a refers to the ground state and ψ_a' to the excited electron configuration on ligand a.

However, a satisfactory band analysis results in a total of four gaussian curves suggesting more than two transitions. Even a small π bonding between the central metal and the acetylacetonate ligand would change the electronic system in such a way that four excited states (two of type A and B, respectively) would arise, leading to a situation which is identical with that discussed for the titanium compounds, where π-electron delocalization is significant. For minor π-electron bonding these energy levels lie closer together and the total splitting of the band maxima does not exceed 4.3 × 10^3 cm^{-1} compared to (11–12) × 10^3 cm^{-1} for the titanium compounds. The band at 29.8 × 10^3 cm^{-1} in the Sn(acac)$_2$I$_2$ spectrum is explained, with use of the concept of optical electronegativities,[33] by a charge-transfer transition of iodide π electrons to empty tin orbitals. The assignment of the bands as weakly perturbed $\pi-\pi^*$ transitions is supported by the small variation in the total oscillator strength, which is almost constant in the Sn(acac)$_2$X$_2$ series, except for the iodo complex, where the oscillator strength is slightly increased. Unlike to the result obtained for the titanium series, a change of the halogen-metal bond scarcely affects the $\pi-\pi^*$ transitions within the acetylacetonate ligands, primarily because of their localization on the two ligands. The total oscillator strength of each Sn(acac)$_2$X$_2$ is lower than the oscillator strength of two free acetylacetonate molecules (2 × 0.36)[6] and also smaller than that of Sn(acac)$_3^+$ (1.1–1.3),[36] but comparable to other closed-shell tris(acetylacetonates).[6] For entirely localized π bonding the dipole strength of acetylacetonate can be considered to be unchanged on ligation.[7]

Judging by the spectra obtained for the germanium and the zirconium complexes, both compounds fall in the regime of smaller π bonding, with electrons being well localized on the ligands. However, the spectrum of the zirconium complex was not completely reliable due to its facile decomposition in solution. In particular, the band at 36.5 × 10^3 cm^{-1} is doubtful and is attributable to hydrolysis products which increased in concentration relatively rapidly during the time it took to record the spectrum. In any case, the crude absorption spectrum and, even more so, the reflectance spectrum suggest a weak to moderate π bonding. This is in contrast to NMR results, which have been explained by significant metal-ligand π bonding in all members of the series of Ti, Zr, and Hf compounds.[19] However, from optical electronegativities only a small degree of π bonding is apparent, on the same order as in tin and germanium complexes: zirconium (χ_{opt} = 1.6), tin (χ_{opt} = 1.5), and germanium (χ_{opt} = 1.45) have, unlike titanium (χ_{opt} = 2.05), similar optical electronegativities, leading to charge-transfer states which are higher in energy and thus a smaller intermixing into π-electron states and a metal-ligand π bonding which is lower for this series of compounds than for the titanium complexes.

The presence of five bands in the spectrum of Ge(acac)$_2$Cl$_2$ instead of four is explained by an admixture of trans isomers in solution. From NMR measurements an equilibrium between cis and trans configurations has been suggested, with a concentration of trans component of 15–20%.[20] If the band at 32.4 × 10^3 cm^{-1}, which has an oscillator strength lower than all the others, is assumed to be due to the impurity, with equal transition probabilities for the two geometries, a contribution of ~14% of the trans isomer is calculated. The fact that the CD spectrum of [Ge(acac)$_3$]$^+$ shows only two absorptions[8] does not necessarily mean that metal-ligand π bonding is not operative in this compound. The band contours in this spectrum deviate from gaussian and should be subject to a band analysis. Symmetry considerations lead for the delocalized system to a maximum of two A$_2$ and three E transitions from the ground

state, all of which are symmetry allowed for electric and magnetic dipole radiation.

The energy shifts exhibited by the absorption peaks within the series of homologous complexes, M(acac)₂X₂, also support the present assignment. Halogen substitution, from fluorine to iodine, decreases the effective charge on the central metal. SCF–CI calculations on acetylacetonate, with a positive charge as an outside perturbation, simulating the central ion, predict a low-energy shift of the first $\pi_3 \rightarrow \pi_4^*$ transition if the central metal charge is decreased.[6] This trend can be observed for all bands within the tin and the titanium series of compounds; in any case respective band components (cf. Table III) move to smaller wavenumbers upon substitution of halogens being able to form a bond of higher covalency. The observed shifts are not explained by a charge-transfer mechanism. An electron transfer from the acetylacetonate ligand to the metal center would be energetically favored for an increased positive charge on the metal. Fluoride ligands, therefore, would facilitate this transition, and complexes with chloride, bromide, etc. ligands would need more energy for this charge-transfer mechanism. However, the experimental results are opposite to this trend. An improved metal–acetylacetonate π bonding with higher effective charges on the metal[18] does not overcome the Coulomb attraction due to the central metal ion, since it is an off-diagonal perturbation in the bond matrix which is of second order with respect to the diagonal valence-state atomic orbitals. If the low-energy band in the titanium compounds would be charge transfer, the main π–π* band at $(37–40) \times 10^3$ cm⁻¹ should be split due to π bonding. However, the spectra of Figure 1 do not show any indication for this. From these reasons an interpretation of the observed bands through a charge-transfer mechanism can be rejected.[18] Predominant π-electron transfer from acetylacetonate to the

central metal must be expected at higher energy. The optical electronegativity parameter for acetylacetonate, which has been set equal to 2.7,[11] should be corrected to a value significantly higher than 3; this parameter probably lies close to the value of other oxygen-donating ligands such as H₂O, acetate, or oxide, for which parameters of about 3.5 are derived.[33,37]

Conclusions

A comparison of optical spectra within a series of homologous complexes of closed-shell metal ions furnishes some evidence for establishing more reliable assignments of the measured absorption peaks. The problem of assigning the bands to π–π* or charge-transfer mechanism and the breakdown of this classification due to π-electron delocalization over the whole molecule can be discussed with use of optical electronegativities of the central atom. Large metal electronegativities favor intermixing of charge transfer into π-electron states, which is the equivalent of increasing the metal–ligand π bonding. Enhanced metal–acetylacetonate π bonding, in turn, leads to a larger splitting of the π–π* band components. The use of these relations may assist in spectral assignments from band splittings for other series of complex compounds, e.g., for open-shell metal ions.

Registry No. Ge(acac)₂Cl₂, 17112-69-5; Sn(acac)₂F₂, 25426-91-9; Sn(acac)₂Cl₂, 16919-65-6; Sn(acac)₂Br₂, 16919-66-7; Sn(acac)₂I₂, 16919-67-8; Ti(acac)₂F₂, 16986-93-9; Ti(acac)₂Cl₂, 16986-94-0; Ti(acac)₂Br₂, 16986-95-1; Zr(acac)₂Cl₂, 19555-94-3.

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Photoelectron Spectra of and Molecular Orbital Calculations on (η⁵-Cyclopentadienyl)dinitrosylhalochromium and -tungsten

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The gas-phase ultraviolet photoelectron spectra are reported for the compounds (η⁵-C₅H₅)M(NO)₂X, where M = Cr, W and X = Cl, Br, I. The observed spin–orbit splitting on the heavy atoms is used to assign and interpret the spectra. The results compare favorably with a Fenske–Hall molecular orbital calculation on the (η⁵-C₅H₅)Cr(NO)₂Cl species. Although the complexes are formally M(0) d⁶, the calculations suggest that the "metal" electrons are highly delocalized onto the nitrosyls. This suggestion is supported by the similarity in the ionization energies of the chromium complexes to those of the isoelectronic (η⁵-C₅H₅)Fe(CO)₂X systems. Comparison of the ionization energy of the metal–halogen σ bonds suggests stronger W–X bonds than Cr–X bonds, which is consistent with the reactivity of the complexes and with the relative metal–chloride bond lengths.

Introduction

Although (η⁵-C₅H₅)Cr(NO)₂Cl was first reported in 1956,[1] it was not until recently that improved synthetic procedures have led to detailed studies on the entire series of chromium, molybdenum, and tungsten derivatives.[2,3] These studies have revealed considerable chemical and structural differences between the chromium and tungsten species. Upon reaction with AgBF₄, CpCr(NO)₂Cl (Cp = η⁵-C₅H₅) goes smoothly to the 16-e complex [CpCr(NO)₂]BF₄, but CpW(NO)₂Cl does not react unless a donor, D, is present in which

case the product is [CpW(NO)₂D]BF₄.[2] Also, the chromium complexes can be alkylated with CH₃MgI while the tungsten complexes cannot.[2] This difference in reactivity could be due to a difference in the M–Cl bond strength, in the relative size of the metals, or in their respective stability at low coordination number and electron count. Recent X-ray crystal structures of CpM(NO)₂Cl (M = Cr, W) have shown the two complexes to be isostructural.[3] The Cr–Cl bond distance was 2.321 (1) Å while the W–Cl bond distance was 2.386 (3) Å. Compared to the M–Cp and M–N distances, the W–Cl distance is short relative to the Cr–Cl distance. This result was interpreted as indicating an exceptionally weak Cr–Cl bond; however, the Mn–Cl bond distance in Mn(CO)₅Cl is 2.367 Å.[4] It may be that the Cr–Cl

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