transition energies of the heteronuclear cluster, as is observed in Ti/Cr/DC510,[11] in Cr/Mo/Ar,[8] and also in a wide range of heterobinuclear metal carbonyl cluster complexes.[25]

While these species are growing, the bis(arene)titanium is decaying, as is indicated by the decrease of the 355-nm band (Figure 10). Although the decrease may be rationalized in terms of the reaction Mo + $(\text{arene})_2\text{Ti} \rightarrow (\text{arene})_2\text{TiMo}$, it is possible that the presence of excess molybdenum brings about the autocatalytic decomposition of $(\text{arene})_2\text{Ti}$, by analogy with the effect of excess titanium on $(\pi\text{-C}_6\text{H}_6)_2\text{Ti}$.[26] That the reverse process does not occur can be seen from the invariance of the absorptions of the polymer-supported molybdenum species (n = 1–5) when titanium vapor is allowed to react at 250 K with a molybdenum-saturated DC510 polymer film (Figure 11) generated also at 250 K. The only observable effect is the monotonic growth of an absorption around 240 nm attributed to a bulklike optical resonance of a Ti_x or Ti_xMo_y cluster of colloidal dimensions.

Therefore it is possible to stabilize small unimetallic and bimetallic clusters at close to room temperature by means of a fluid polymer matrix. Furthermore, it is possible to modify the macroscale reactions of DC510 to allow the isolation of a polymer containing both the bis(arene)metal complex and cluster species. It is now our task to find a way to investigate the catalytic activity of these unique cluster species.

Acknowledgment. We wish to acknowledge the financial assistance of the Natural Sciences and Engineering Council of Canada, Imperial Oil, Erindale College, and Lash Miller Chemical Laboratories.

Registry No. Mo, 7439-98-7; Ti, 7440-32-6; DC510, 63148-53-8.

---

(25) H. B. Abrahamson, C. C. Frazier, D. S. Ginley, H. B. Gray, J. Lilienthal, D. R. Tyler, and M. S. Wrighton, *Inorg. Chem.*, **16**, 1554 (1977).

(26) M. T. Anthony, M. L. H. Green, and D. Young, *J. Chem. Soc., Dalton Trans.*, 1419 (1975).

(27) S. Mitchell and G. A. Ozin, *Inorg. Chem.*, **16**, 3063 (1977).

(28) H. Huber, P. Mackenzie, and G. A. Ozin, *J. Am. Chem. Soc.*, in press.

(29) R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

Contribution from the Department of Chemistry,
Youngstown State University, Youngstown, Ohio 44555

High-Pressure Mass Spectra and Gaseous Ion Chemistry of Metal β-Diketonates with Bulky Substituents

STEVEN M. SCHILDCROUT

Received June 18, 1979

Mass spectra at normal and elevated pressures are reported and interpreted for chelates of 2,2,6,6-tetramethyl-3,5-heptanedione anion with Cr(III), Fe(III), Co(II), Co(III), Ni(II), Cu(II), Zn(II), and Al(III). At the higher pressures in each case primary positive fragment ions undergo gaseous bimolecular reaction with the neutral mononuclear complexes to form heavier polynuclear positive ions usually with unfragmented ligands. These are analogous to those previously observed for chelates of sterically less hindered β-diketone ligands. Competing with the association reaction in most cases is charge transfer between fragment ions and the neutral complex. Although they are known to prevent intermolecular association in condensed phases, the *tert*-butyl groups on the present complexes are found to hinder, but not prevent, gaseous ion/neutral association in the tetrahedral and octahedral complexes. There is no significant hindrance for the planar complexes. The *tert*-butyl substituents tend also to enhance charge transfer. In the absence of steric hindrance and charge transfer, the tendency to undergo ion/neutral association follows the polarizability or basicity of the ligand. The tendency of the metal to maintain its preferred oxidation state determines which of the possible polynuclear ions will form. These heavy ions are considered to be Lewis acid/base complexes rather than van der Waals complexes.

Introduction

Previous studies of gaseous positive ion/neutral reactions of organometallic complexes have involved mainly metallocenes and their derivatives and have used the techniques of chemical ionization,[1] high-pressure mass spectrometry,[2,3] and ion cyclotron resonance spectrometry.[4–6]

Another class of complexes amenable to such studies consists of the metal acetylacetonates, which have been investigated in this laboratory by using high-pressure mass spectrometry. Reaction of the neutral monomeric vapor with its positive molecular and fragment ions was found to give high abundances of a variety of heavy, polynuclear ions at ion-source pressures up to 10^{-2} torr.[7] The observation of these product ions raises the need to elucidate their structure and to rationalize the preferential formation of certain such ions from certain precursors.

Neutral metal complexes of the conjugate base of 2,2,6,6-tetramethyl-3,5-heptanedione (thd^-)[8] are similar in molecular structure to those of acetylacetone and, because of their high volatility and thermal stability,[9,10] have been used in gas chromatography and chemical ionization[11] for analysis of metals. The low-pressure positive[12,13] and negative ion[14] mass

---

(1) Hunt, D. F.; Russell, J. W.; Torian, R. L. *J. Organomet. Chem.* **1972**, *43*, 175.

(2) Schildcrout, S. M. *J. Am. Chem. Soc.* **1973**, *95*, 3846.

(3) Müller, J.; Holzinger, W.; Kalbfus, W. *J. Organomet. Chem.* **1975**, *97*, 213, and preceding papers in the series.

(4) Foster, M. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 4814.

(5) Corderman, R. R.; Beauchamp, J. L. *Inorg. Chem.* **1976**, *15*, 665; *J. Am. Chem. Soc.* **1976**, *98*, 3998; *Inorg. Chem.* **1978**, *17*, 68.

(6) Hemberger, P. H.; Dunbar, R. C. *Inorg. Chem.* **1977**, *16*, 1246.

(7) Schildcrout, S. M. *J. Phys. Chem.* **1976**, *80*, 2834.

(8) Hthd is known also as dipivaloylmethane or hexamethylacetylacetone. Other abbreviations used here are acac^- for the acetylacetonate and hfac^- for the hexafluoroacetylacetonate ligand. Ligands are bidentate via the oxygen atoms.

(9) Berg, E. W.; Herrera, N. M. *Anal. Chim. Acta* **1972**, *60*, 117.

(10) Yoshida, I.; Kobayashi, H.; Ueno, K. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4061; *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2203.

(11) Prescott, S. R.; Campana, J. E.; Jurs, P. C.; Risby, T. H.; Yergey, A. L. *Anal. Chem.* **1976**, *48*, 829. Prescott, S. R.; Campana, J. E.; Risby, T. H. *Ibid.* **1977**, *49*, 1501.

(12) McDonald, J. D.; Margrave, J. L. *J. Less-Common Met.* **1968**, *14*, 236.

Table I. Relative Abundances of Major Ions in the Low-Pressure 70-eV Mass Spectra of thd Complexes[a]

complex	ML_3^+	ML_2^+	$(ML_2 - Bu)^+$	ML^+
CrL_3	38 (601)	30 (418)	5 (361)	12 (235)
FeL_3	7 (605)	70 (422)	11 (365)	6 (239)
CoL_3	15, 25[b] (608)	41, 28[b] (425)	27, 28[b] (368)	15, 10[b] (242)
AlL_3	8, 5[b] (576)	75, 75[b] (393)		
CoL_2		22 (425)	61 (368)	12 (242)
NiL_2		43, 40[c] (424)	55, 52[c] (367)	
CuL_2		10 (429)	26 (372)	5 (246)
ZnL_2		21 (430)	70 (373)	10 (247)

[a] Abundance is given as percent of total abundance of metal-containing ions and is followed in parentheses by the nominal *m/z* value for the predominant isotopic peak. M = metal and L = thd. See text for other ions unique to certain complexes. [b] Abundance from ref 12 for 50 eV. [c] Abundance from ref 13 for 70 eV.

Table II. Maximum Relative Abundances of Nonprimary Ions in the High-Pressure Mass Spectra of thd Complexes[a]

complex	ML_2^+	ML_3^+	$M_2L_2^+$	$M_2L_3^+$	$M_2L_4^+$	$M_2L_5^+$	$M_3L_4^+$	$M_3L_5^+$
CrL_3		s (601)			w (836)	w (1019)		
FeL_3		m (605)		w (661)	w (844)	m (1027)		
CoL_3		s (608)		w (667)	w (850)	*b*		
AlL_3		*c*				w (969)		
CoL_2				s (667)	w (850)		w (909)	
NiL_2	m (424)		w (482)	m (665)	w (848)		w (906)	
CuL_2	m (429)		m (492)	s (675)			m (921)	w (1104)
ZnL_2				s (677)	m (860)			

[a] s = strong, more than 30% of total abundance for metal-containing ions; m = medium, between 10 and 30%; w = weak, less than 10%. Numbers in parentheses are the nominal *m/z* values for the predominant isotopic peaks. M = metal and L = thd. [b] $Co_2(thd)_5^+$ is not detected, but $[Co_2(thd)_5 - Bu]^+$ is w (976) from $Co(thd)_3$. [c] Variation of the abundance of $Al(thd)_3^+$ with pressure is too small to determine whether it is a secondary ion.

spectra of several of these complexes have been reported. Since steric hindrance by the *tert*-butyl substituents on the ligand prevents neutral molecular association in solution and in the crystal state,[15] neither should there be such association in the gas phase. A knowledge of the tendency, if any, of these complexes to undergo ion/neutral association in the gas phase should help in deducing the structure of the associated ions of these complexes and of their acac analogues. Observation of such ions from thd complexes would indicate even more strongly than in the cases of acac and hfac that these polynuclear ions arise from ion/neutral reaction rather than from electron-impact-induced unimolecular decomposition of supposed neutral polymers in the vapor.

The present work was undertaken to extend the previous study of acac and hfac chelates[7] to include now eight thd chelates with various geometries[15] and central metal atoms, viz., the tetrahedral complexes of Co(II) and Zn(II), the planar complexes of Ni(II) and Cu(II), and the octahedral complexes of Al(III), Cr(III), Fe(III), and Co(III), to determine low-pressure positive ion mass spectra where they have not been reported previously, and to determine whether the *tert*-butyl substituents inhibit ion/neutral reaction by their steric hindrance or enhance it by their high polarizability compared to those of the acac and hfac complexes.

Experimental Section

The thd complexes were synthesized from purchased Hthd and metal salts by using published procedures.[9,16] Chloride salts were used in each case except for Zn(II) and Co(II), where the acetate was used, and Co(III), where $CoCO_3$ was treated with Hthd and H_2O_2. Products were identified by color, melting point, and mass spectrum. The melting point of $Cu(thd)_2$ is found to be 188–189 °C in agreement with that reported by Cotton and Fackler[17] although others[9,10,16] have reported different values.

The CEC (Du Pont) 21-491 mass spectrometer[2] and its operating conditions, the method of sample introduction, and the method of data interpretation[7] are described elsewhere.

Results

The low-pressure mass spectra show types of ions common to several or all of the thd complexes studied. These are given in Table I and consist of the molecular ion and fragments corresponding to loss of neutral thd and/or butyl radical. Other types of fragment ions detected for certain complexes are discussed in the next section.

As the pressure of the sample vapor in the ion source is raised, each of the eight thd complexes shows di- or trinuclear ions corresponding to products of ion/neutral association reactions, although this is very slight for $Al(thd)_3$. For all complexes except those of Co(II), Zn(II), and possibly Al(III), an increase is detected in the relative abundance of the molecular ion consistent with bimolecular charge transfer between fragment ions and the neutral vapor. These qualitative results are compared in Table II.

Discussion

The overall results for the thd complexes appear similar to those for the acac and hfac complexes[7] in that polynuclear ions form readily in most cases as ion-source pressure is raised, with little fragmentation of coordinated ligands. Each complex is now considered in the order listed in Tables I and II.

$Cr(thd)_3$. Besides the ions shown in Table I, the low-pressure spectrum includes 15% $HCr(thd)_2^+$ at *m/z* 419, which may result from rearrangement or more likely from thermal reaction with impurities at the ion-source temperature of 170 °C; slight residue was noted in the sample-holding tube following sublimation into the mass spectrometer. The abundance of this ion decreases as pressure is raised, as expected for a primary ion.

The dinuclear secondary ions $Cr_2(thd)_4^+$ and $Cr_2(thd)_5^+$ each increase with pressure to 8%, which is much less than observed for the analogous ions from $Cr(acac)_3$. This is a result of competition from charge transfer between the abundant fragment $Cr(thd)_2^+$ and $Cr(thd)_3$, which causes growth in $Cr(thd)_3^+$ to 70% at the higher pressures. In the case of $Cr(acac)_3$ this charge transfer was not observed and

---

(13) Macdonald, C. G.; Martin, R. L.; Masters, A. F. *Aust. J. Chem.* **1976**, *29*, 257.
(14) Garnett, J. L.; Gregor, I. K.; Guilhaus, M. *Org. Mass Spectrom.* **1978**, *13*, 591.
(15) Holum, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.
(16) Hammond, G. S.; Nonhebel, D. C.; Wu, C.-H. S. *Inorg. Chem.* **1963**, *2*, 73.
(17) Cotton, F. A.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 2818.

was assumed to be endothermic.[7]

That reaction of the type

$$ML_2^+ + ML_3 \rightarrow ML_2 + ML_3^+$$

occurs when L = thd but not acac indicates that the ionization energy of ML_3 is less than that of ML_2 only when L = thd. The ionization energies of β-diketonate metal complexes have been found to depend strongly on the nature of the ligand, and the electronic effect expected from the *tert*-butyl groups in the thd complexes should lower their ionization energies relative to those of the acac complexes,[18] as reported for FeL_3 and HL.[19] The present results show that this effect is greater for CrL_3 than CrL_2, and it seems reasonable that three ligands have more of an effect than two if ionization involves delocalized ortibals or metal orbitals strongly influenced by the ligand.

Fe(thd)$_3$. As with Fe(acac)$_3$, the low-pressure base peak here is due to FeL_2^+. Not shown in Table I is the ion $[Fe(thd)_3 - Bu]^+$ at *m/z* 548 with 5% abundance.

As sample pressure is raised by heating to 135 °C, the secondary ions $Fe_2(thd)_x^+$, where x = 3, 4, and 5, grow in abundance to 2%, 9%, and 19%, respectively. Ions analogous to the latter two are observed for Fe(acac)$_3$[7] and for Cr(thd)$_3$ as discussed above. In the Fe complexes, as with Cr, the dinuclear ions are less abundant with thd than with acac. This results from charge transfer in the case of thd causing secondary $Fe(thd)_3^+$ to increase with pressure to 30% of total abundance of metal-containing ions.

The equilibrium vapor pressure of Fe(thd)$_3$ at 135 °C is calculated to be 10^{-1} torr from data previously reported.[20] The sample pressure in the ion source can be no greater than this, which is consistent with the estimate that present conditions of the apparatus permit sample pressures not greater than 10^{-2} torr, as already stated.

Co(thd)$_3$. The low-pressure mass spectrum measured here is consistent with one given for 50 eV. The previous workers[12] reported 5% $[Co(thd)_3 - Bu]^{2+}$ at *m/z* 275.5, which is now observed at an uncertain but lower abundance.

Heating the sample toward the ion-source temperature of 170 °C results again in pressures at which secondary ions are observed. The dinuclear ions $Co_2(thd)_3^+$, $Co_2(thd)_4^+$, and $[Co_2(thd)_5 - Bu]^+$ have abundances no greater than 6%, 7%, and 1%, respectively. $Co_2(thd)_5^+$ is not found. As in the above cases, the molecular ion is formed by charge transfer, growing to 70% abundance. Similar charge transfer was observed for Co(acac)$_3$[7] but to a lesser extent than for Co(thd)$_3$.

Al(thd)$_3$. The present results confirm the main features of the low-pressure spectrum as reported by McDonald and Margrave[12] except for an ion of 5% abundance assigned by these workers as *m/z* 378 or $[Al(thd)_2 - CH_3]^+$, which is now found instead at *m/z* 377 corresponding to the rearrangement ion $[Al(thd)_2 - CH_4]^+$ with 6% abundance. The latter assignment seems to be reasonable when one considers that the even-electron ion $Al(thd)_2^+$ should tend to fragment into an ion and a neutral, each with an even number of electrons, rather than to lose CH_3 radical, producing two odd-electron fragments. Elimination of methane from a *tert*-butyl group leaves a 2-propenyl group conjugated with the pseudo-aromatic chelate ring while the Al atom maintains its preferred oxidation state of +3. The mass spectrum of *tert*-butylbenzene[21] provides an analogy, where the base peak is assigned to the even-electron ion formed by loss of CH_3 radical from the molecular ion but where subsequent loss of another CH_3 radical occurs to a lesser extent than loss of CH_4.

Other minor primary ions not listed in Table I include 3% $[Al(thd)_3 - Bu]^+$ at *m/z* 519, 5% $[Al(thd)_2 - C_2H_6]^+$ at *m/z* 363, and 3% $[Al(thd)_3 - C_8H_{18}]^{2+}$ at *m/z* 231. The last is of interest in that the singly charged analogue at *m/z* 462 is not observed, suggesting formation of this ion by loss of $C_4H_9^-$ from $[Al(thd)_3 - Bu]^+$. These ions were reported previously in the 50-eV spectrum[12] with somewhat different abundances.

Raising the sample pressure by heating to 120 °C yields only a trace (0.2%) of $Al_2(thd)_5^+$ with no other secondary ions detected. The dominance of $Al(thd)_2^+$ at all pressures makes it difficult to detect pressure dependence for the other ions, and no conclusion is made concerning possible formation of $Al(thd)_3^+$ by charge transfer. Similarly Al(acac)$_3$ and Al(hfac)$_3$ showed[7] no charge transfer in their high-pressure spectra, and Al(hfac)$_3$ yielded no detectable $Al_2L_5^+$.

Co(thd)$_2$. Since this complex shows some lability in air, freshly prepared samples are loaded into the mass spectrometer under N_2 atmosphere and are then held under vacuum several hours before mass spectrometric data are obtained. The low-pressure spectrum arises mainly from the three ions indicated in Table I, all of which are important in the Co(thd)$_3$ spectrum also. About 4% of $[Co(thd)_2 - C_4H_8]^+$ at *m/z* 369 is detected; this even-electron ion is rationalized as the rearranged product of butene elimination from the even-electron molecular ion $Co(thd)_2^+$. As Table I indicates, loss of neutral C_4H_9 radical occurs to a much greater extent than loss of C_4H_8, presumably because the rearrangement process is at a kinetic disadvantage.

While the sample was heated toward the ion-source temperature of 200 °C, the pressure rise permits formation of the dinuclear ions $Co_2(thd)_3^+$ and $Co_2(thd)_4^+$ as well as the trinuclear $Co_3(thd)_4^+$ with respective maximum abundances of 30%, 5%, and 5%. The previous work[7] showed analogous ions arising from Co(acac)$_2$. Formation of $Co(thd)_2^+$ by charge transfer is not observed.

Ni(thd)$_2$. The dominant primary ions for this complex are the molecular ion and that resulting from loss of C_4H_9 radical by the molecular ion, as indicated in Table I and as previously reported.[13]

When the sample pressure is raised with the ion source at 170 °C, the molecular-ion abundance increases to 57% as a result of charge transfer from the base fragment ion. The secondary ions $Ni_2(thd)_x^+$, where x = 2, 3, and 4, grow in abundance to 9%, 25%, and 2%, respectively, while $Ni_3(thd)_4^+$ grows to 3%. Except for the very weak $Ni_2(thd)_4^+$, all these polynuclear ions have more abundant analogues in the high-pressure spectra of Ni(acac)$_2$, which did not show[7] formation of $Ni(acac)_2^+$ by charge transfer.

Since the growth of $Ni(thd)_2^+$ is not especially great at higher pressures and since no polynuclear ion observed has C_4H_9 missing from a ligand, it would seem that the polynuclear ions arise from reaction of $Ni(thd)_2^+$. Thus

$$Ni(thd)_2^+ + Ni(thd)_2 \rightarrow Ni_2(thd)_x^+ + (4 - x)thd$$

The trinuclear ion would form by reaction of a dinuclear ion with the neutral Ni(thd)$_2$.

Cu(thd)$_2$. The low-pressure mass spectrum has not been previously reported. Besides the ions listed in Table I, the spectrum includes as its strongest peak 37% $[Cu(thd)_2 - 2Bu]^+$ at *m/z* 315, whose analogue is not observed with any of the other thd complexes. Detection of the corresponding metastable decomposition[22] indicates that this ion forms by loss of C_4H_9 radical from the odd-electron ion $[Cu(thd)_2 - Bu]^+$. Also observed is 14% $[Cu(thd) - C_4H_8]^+$ at *m/z* 190.

---

[18] Westmore, J. B. *Chem. Rev.* **1976**, *76*, 695.

[19] Evans, S.; Hamnett, A.; Orchard, A. F.; Lloyd, D. R. *Faraday Discuss. Chem. Soc.* **1972**, *54*, 227.

[20] Brunner, H. R.; Curtis, B. J. *J. Therm. Anal.* **1973**, *5*, 111.

[21] "Selected Mass Spectral Data", Research Project 44; American Petroleum Institute: College Station, Texas, 1953; Serial No. 934.

[22] Such processes are not detected with the present double-focusing instrument unless they occur with high probability between the electric and magnetic sectors.

With the ion source at 150 °C, raising the sample pressure results in the molecular-ion abundance growing to 38% as a result of charge transfer. $Cu_2(thd)_2^+$ grows to 10% before decreasing by subsequent reaction at higher pressure. $Cu_2(thd)_3^+$, $Cu_3(thd)_4^+$, and $Cu_3(thd)_5^+$ grow to 39%, 17%, and 1%, respectively. Not shown in Table II is $[Cu_2(thd)_3 - Bu]^+$ at *m/z* 618, which grows to 5% and then decreases as pressure increases.

Despite significant charge transfer in $Cu(thd)_2$, this complex shows polynuclear ion formation to a greater extent than $Cu(acac)_2$ or $Cu(hfac)_2$, which do not show charge transfer.[7]

$Zn(thd)_2$. Low-pressure spectra show significant abundances of only the three ions indicated in Table I. Very low abundances of $[Zn(thd) - CH_4]^+$ at *m/z* 231 and $HZn(thd)_2^+$ at *m/z* 431 are detected. The latter is attributed to an impurity, evidenced also by a white residual film observed in the sample tube after sublimation.

High-pressure spectra obtained with the ion source near 130 °C show $Zn_2(thd)_3^+$ increasing in abundance to 53% and $Zn_2(thd)_4^+$ increasing to 14%. There is no evidence of formation of $Zn(thd)_2^+$ by charge transfer. Equilibrium vapor pressure data for this complex[20] are consistent with the pressure estimates already mentioned.

The maximum abundance for $Zn_2L_3^+$ when L = thd is close to that when L = acac.[7]

Conclusions

The observation of substantial abundances of polynuclear ions in the high-pressure mass spectra of these thd complexes confirms the earlier conclusion that such ions in the spectra of metal β-diketonates arise from ion/neutral reaction of mononuclear species.[7] A neutral polymeric vapor should not exist for any thd complex with its bulky substituents,[15] so dissociative fragmentation of such a vapor to produce the polynuclear ions is precluded here as it was for the transition- and post-transition-metal complexes of acac and hfac previously studied.

The polynuclear ions formed from the thd complexes are similar to those found with the other β-diketonates in that they typically contain unfragmented ligands in such number that the apparent oxidation state of the metal is the same as in the original complex or as in the common condensed-phase chemistry of the metal. Thus the M(II) state in ML_2 is maintained in $M_2L_3^+$ and $M_3L_5^+$ while the ML_3 complexes keep M(III) in $M_2L_5^+$. $M_3L_8^+$, which may thus be expected from ML_3, would be beyond the upper mass limit of the present instrument.

Charge transfer between neutral vapor and ionic fragments accounts for enhancement of the molecular ion abundance at higher pressures in the cases of the thd complexes of Cr(III), Fe(III), Co(III), Ni(II), and Cu(II). This implies that the ionization energy for each of these complexes is less than the recombination energy of at least one of its abundant fragment ions. $Co(acac)_3$ was the only acac or hfac analogue to show such charge transfer,[7] so it is seen that the thd ligand favors this process as discussed above for the case of Cr(III). To the extent that charge transfer is favored for the thd complexes, the competing formation of polynuclear ions must be impeded although still important. Under similar conditions the chief fragment ion of ferrocene was found to undergo charge transfer at a rate about 6 times that of the competing dinuclear ion formation.[2]

An inferential consideration of possible structures for the polynuclear ions should distinguish between the possibilities that these ions result from a chemical association or from one involving only van der Waals interaction. The latter seems unlikely since the $M(thd)_2$ complexes do not show an ion $[M_2(thd)_4 - Bu]^+$ at high pressures although each gives $[M(thd)_2 - Bu]^+$ as an abundant fragment.

In those cases with insignificant charge transfer the tendency to form polynuclear ions should follow the trend in polarizability, thd > acac > hfac for the same metal, if only van der Waals association were involved. The same order would be expected if heavy-ion formation were determined by the basicity of the chelate. This order has been reported for pK_a of the acidic ligands in solution[23] in agreement with expected inductive effects. Comparing the previous[7] and the present results, it is seen that the abundances of polynuclear ions from CoL_2, ZnL_2, and AlL_3 are, respectively, acac > thd, acac ≈ thd, and acac > thd > hfac. For CuL_2, thd > acac ≈ hfac is found despite competition from charge transfer in $Cu(thd)_2$ only. While a highly polarizable molecule should have an enhanced rate of collision with ions, steric or other chemical effects must also be considered in accounting for rates of polynuclear ion formation for thd vs. acac complexes.

For those cases where charge transfer does not successfully compete with heavy-ion formation, the latter process occurs at least as readily in the acac complex as in the thd complex of the same metal, except for CuL_2, the only such case with planar coordination about the metal. This implies that there is steric hindrance to polynuclear-ion formation in thd complexes except for the case of planar coordination about the metal, where the ligand ring is more accessible to an incoming ion than in tetrahedral and octahedral complexes. This is consistent with molecular models and with results reported for the relative tendencies of octahedral CrL_3 to undergo gaseous protonation, which occurs in the order acac > thd > hfac.[11] For the planar case, polarizability or inductive effects determine reactivity.

Possible basic sites on the ligand in a neutral complex are the enolic carbon atom, the oxygen atoms, and the delocalized π system of the ring. The first seems least likely for the thd complexes since it is the most blocked by the *tert*-butyl groups. Although the *tert*-butyl groups in neutral thd complexes may prevent the oxygen-bridged polymerization that occurs in their absence in condensed phases,[24] this need not be so for gaseous ion/neutral association. The acidic site on the ion is apparently the partially coordinated metal atom.

Acknowledgment. The author thanks Nassim H. Khatib and Michael T. Bell for preparing the metal complexes.

Registry No. $Cr(thd)_3$, 14434-47-0; $Fe(thd)_3$, 14876-47-2; $Co(thd)_3$, 14877-41-9; $Al(thd)_3$, 14319-08-5; $Co(thd)_2$, 13986-53-3; $Ni(thd)_2$, 14481-08-4; $Cu(thd)_2$, 14040-05-2; $Zn(thd)_2$, 14363-14-5.

---

(23) Yokoi, H. *Inorg. Chem.* **1978**, *17*, 538.

(24) Yoshida, I.; Kobayashi, H.; Ueno, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1411.