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INFRARED AND MASS SPECTRAL STUDIES OF COMPLEXES OF BIS(HEXAFLUOROACETYLACETONATO)METAL(II) WITH 1,10-PHENANTHROLINE

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Mixed ligand complexes of the type $M(hfa)_2phen$ were prepared and IR, DTA-TG and MS were measured in order to investigate the stabilities of these complexes. Exceptional properties were observed for the Cu(II) complex on IR and MS measurements. The marked weakening of Cu-O bonds in the Cu(II) adducts is ascribed to the Jahn-Teller effect.

Bis(β-diketonato)metal(II) complexes behave as Lewis acids and form five- or six-coordinate adducts with neutral donor molecules$^{1)}$. Most of the studies on the resulting base adducts have been concerned with the six-coordinate 1:2 ones with unidentate nitrogen bases such as pyridine(py). It was recently found that bidentate neutral ligands add to metal(II) β-diketonates to form cis-octahedral adducts more stable than those of unidentate donors owing to the chelate effect$^{2-4)}$. However, only Cu(II) complexes have been referred to in these reports, and the structures as well as the properties of the adducts of other metal chelates should be investigated in some detail.

The present paper describes the infrared(IR) and the mass spectra(MS) of the adducts of the type: $M(hfa)_2phen$ [M = Co(II), Ni(II), Cu(II) and Zn(II); Hhfa = hexafluoroacetylacetone; phen = 1,10-phenanthroline], which are considered to be most stable because of both the presence of the highly electron-withdrawing CF_3- groups and the chelate effect by phen. The DTA-TG method was also applied to Cu(II) complexes in order to obtain informations on the thermal stabilities of these adducts.

Experimental

$M(hfa)_2$ and $Cu(hfa)_2(py)_2$ were prepared according to the methods described in the literatures$^{5,6)}$. Preparation of $M(hfa)_2phen$: $M(hfa)_2$ and phen were dissolved in a 1:1 molar ratio in warm methanol. After standing overnight, crystallized $M(hfa)_2phen$ was filtered and dried over P_2O_5 under reduced pressure.

IR spectra were measured by using the same technique as written in the previous paper$^{7)}$. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6D single focussing mass spectrometer according to a direct inlet system under the following conditions: ion source temperature 300 °C, ionization voltage 30 V, ion accelerating voltage 3 kV, ionization current 300 μA. DTA-TG curves were recorded simultaneously at the heating rate of 5 °C/min in static air using a Rigaku TG-DTA Standard Type.

Results and Discussion

Fig. 1 shows the far IR spectra of M(hfa)$_2$phen together with Cu(hfa)$_2$(py)$_2$, in which five metal-sensitive bands were observed in the 300-700 cm^{-1} region. It is generally known that in a series of isostructural complexes, substitution of a metal ion by another leads to a remarkable shift in metal-ligand stretching frequencies$^{8)}$. Therefore, these five bands are considered to contain ν(M-O) character to a varying degree and those within the range of 370-400 cm^{-1} are assigned to the least-coupled ν(M-O) bands, because they exhibit the maximum sensitivity to the metal ions.

The IR spectra of M(hfa)$_2$ also show the corresponding five bands in the same region, and the ν(M-O) frequencies of the most metal-sensitive bands follow the Irving-Williams stability order, viz. Co 398 $<$ Ni 404 $<$ Cu 420 $>$ Zn 385. On the other hand, the ν(M-O) frequencies of the phen adducts decrease in the following order: Ni 393 $>$ Co 387 $>$ Cu 379 $>$ Zn 374. The above bands are shifted towards the lower frequencies upon the coordination of phen, the magnitudes of shifts being 11 cm^{-1} for Co(II), Ni(II), Zn(II) complexes and 41 cm^{-1} for Cu(II).

These shifts may generally be explained in terms of the electrostatic repulsion between ligands. Anhydrous M(hfa)$_2$ are estimated to have a polynuclear octahedral geometry (M = Co, Ni and Zn) or a square planar one (M = Cu) like acetylacetonate analogues of these metals$^{1)}$. A considerable "crowding" of donor ligands exists in the six-coordinate complex of a first transition metal(II). Thus, the coordination of more basic phen molecule in place of bridging oxygen atoms leads to the increased repulsion between β-diketonate ions around the central metal, so that M-O distances are slightly lengthened.

In the case of the Cu(II) complex, an exceptionally large shift of 41 cm^{-1} was observed. There are two possible explanations for this result. One is that the coordination number of Cu(II) changes from four to six upon the adduct formation. Increased coordination number generally causes a considerable low-frequency shift of metal-ligand stretching band$^{9)}$. However, the shift of 41 cm^{-1} seems to be too large even if the change of coordination number is taken into consideration, since Cu(hfa)$_2$ is assumed not to exist as a completely isolated molecule but to interact weakly with the ring carbon atoms above and below its square plane, as is reported

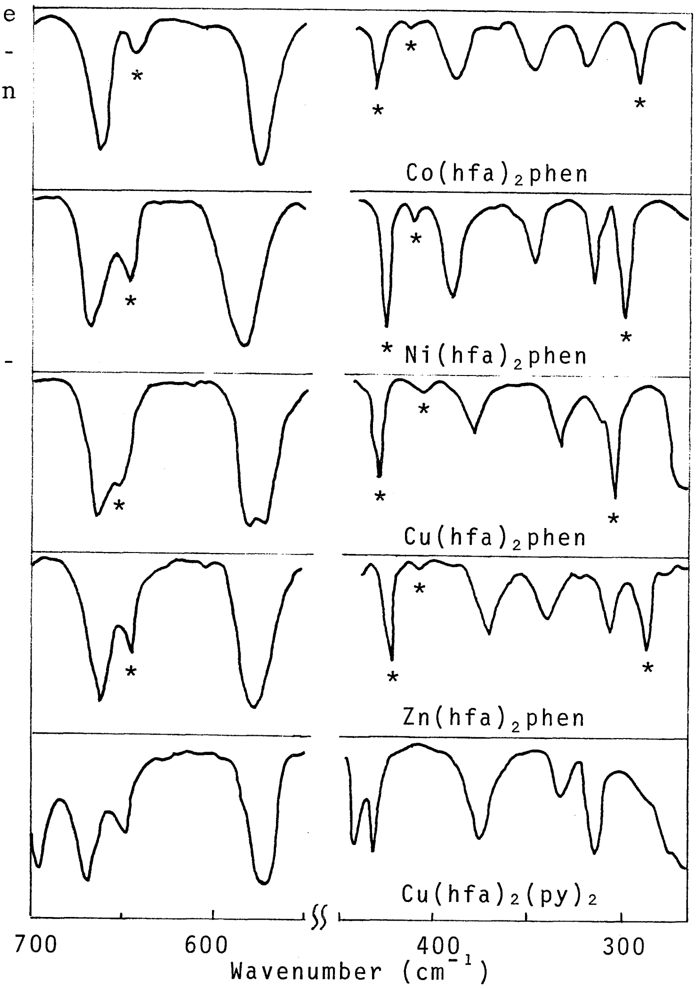

Fig. 1. Far-infrared spectra of M(hfa)$_2$phen and Cu(hfa)$_2$(py)$_2$
* vibration of phen

for bis(acetylacetonato)copper(II)[10].

A more plausible interpretation can be offered by considering a structure that has the Jahn-Teller distortion arising from d^9 electron configuration of Cu(II) ion. The coordinating ability of phen is evidently higher than that of hfa which is the least basic in a series of β-diketonate ions. The significant back-bonding as well as the chelate effect may stabilize the bonds between Cu(II) and phen. It is, therefore, reasonable that phen occupies the equatorial sites, forming a most stable chelate ring with Cu(II). One oxygen atom in hfa also occupies the equatorial position, whereas the other oxygen coordinates along the axial direction, which results in a longer and weaker Cu-O bond than the former. The observed ν(Cu-O) of the phen adduct is considered to exhibit a character intermediate between the long and the short Cu-O bonds because of the vibrational coupling[7].

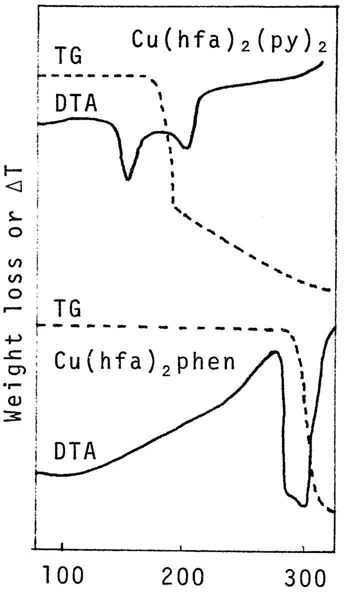

Fig. 2. DTA-TG curves for Cu(II) complexes

The above assumption is supported by the fact that the ν(Cu-O) of $Cu(hfa)_2(py)_2$ appears at an almost identical frequency (376 cm^{-1}) with that of $Cu(hfa)_2phen$, because a similar cis-equatorial structure has been confirmed by single crystal X-ray analysis in $Cu(hfa)_2(py)_2$[11].

The mass spectrometry of $M(hfa)_2phen$ was investigated in order to examine the behavior of the adducts against electron impact. Although mass spectra of metal chelates have been studied extensively, no report has been published on those of base adducts. A series of $M(hfa)_2phen$ is expected to be suitable for this purpose, since these molecules are stable enough to be measured without thermal decomposition.

Table 1 lists the relative intensities of the main fragment peaks in the mass spectra of the phen adducts. No peak due to $[M(hfa)_2]^+$ was detected. It is reported[12] that the mass spectrum of $Cu(hfa)_2$ showed a parent peak, which reveals that the addition of phen affects the fragmentation behavior of the complex seriously. Although the spectra in the m/e region greater than 600 where parent peaks might appear could not be measured because of the limitation of the instrument used, the following fragmentation sequences are assumed:

$$\text{Co, Ni, Zn ; } [M(hfa)_2phen]^+ \xrightarrow[\text{-hfa}]{} [M(hfa)phen]^+ \xrightarrow[\text{-phen}]{} [M(hfa)]^+$$

$$\text{Cu ; } [Cu(hfa)_2phen]^+ \xrightarrow[\text{-hfa}]{} [Cu(hfa)phen]^+ \xrightarrow[\text{-hfa}]{} [Cu\text{-}phen]^+$$

After the loss of one molecule of hfa, $[Cu(hfa)phen]^+$ undergoes a quite different fragmentation from those of the others. That is, in the case of the Cu(II) complex, the remaining hfa is released preferentially, while only the loss of phen occurs in Co(II), Ni(II) and Zn(II) complexes.

Fig. 2 shows the DTA-TG curves for the Cu(II) complexes. $Cu(hfa)_2(py)_2$ begins to evolve pyridine at about 170 °C and gives an inflection in the TG curve at 190 °C, at which temperature the removal of the two pyridine molecules was completed. On the

Table 1. Mass fragmentations of M(hfa)$_2$phen

	Relative intensity			
Ion	Co	Ni	Cu	Zn
$(CO)^+$	1000	465	784	1000
$(CF_3)^+$	130	525	216	450
$(phen)^+$	1000	1000	1000	331
$[M\text{-}phen]^+$	–	–	63,17	–
$[M(hfa)]^+$	72	122,44	–	21
$[M(hfa)phen]^+$	211	243,88	81,25	47,23,25

other hand, Cu(hfa)$_2$phen is thermally stable up to 270 °C, then an endothermic decomposition and evaporation occur simultaneously at about 300 °C to give a carbonized product. From these results, it is revealed that the coordination of phen enhances the thermal stability of the adduct far more exceedingly than that of py, which is mainly ascribable to the chelate effect by the bidentate ligand.

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