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Adducts of Bis(hexafluoroacetylacetonato)metal(II) with Uni- and Bidentate Nitrogenous Bases

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Base adducts of the types: M(hfa)$_2$(py)$_2$, M(hfa)$_2$phen, and M(hfa)$_2$bpy [M=Co(II), Ni(II), Cu(II), and Zn(II); Hhfa=hexafluoroacetylacetone; py=pyridine; phen=1,10-phenanthroline; bpy=2,2′-bipyridine] were prepared, and their infrared spectra were examined in detail. These adducts have a *cis*-octahedral configuration except for Ni(hfa)$_2$(py)$_2$. The metal-oxygen stretching frequencies of the adducts in the 405—370 cm^{-1} region decrease along the series: nickel(II)>cobalt(II)>copper(II)>zinc(II). Adduct formation leads to the marked weakening of Cu–O bonds in the copper(II) adducts, which is ascribable to the equatorial ligation of the neutral bases. The mass spectral studies of M(hfa)$_2$phen and M(hfa)$_2$bpy revealed that the addition of a neutral ligand affects the fragmentation of the complex remarkably. The exceptional behavior of Cu(hfa)$_2$phen under electron impact is explained in terms of the tendency of copper(II) ion to undergo valency change.

Bis(β-diketonato)metal(II) complexes behave as Lewis acids and form five- or six-coordinate adducts with neutral donor molecules.$^{1)}$ The stability of an adduct depends both on the basicity of a β-diketonate and on that of a neutral ligand. Introduction of an electron-withdrawing group such as CF$_3$- into β-diketone increases the affinity of a central metal ion for ligation.$^{2-6)}$ For example, bis(trifluoroacetylacetonato)copper (II) and bis(hexafluoroacetylacetonato)copper(II) form isolable 1:2 adducts with pyridine,$^{2,5,7)}$ whereas bis(acetylacetonato)copper(II) forms only an unstable 1:1 adduct that loses pyridine on exposure to air.$^{8)}$ It is also known that the more basic a neutral ligand is, the more stable the resulting adduct tends to be.$^{9)}$

Most of the studies on base adducts have been concerned with the coordinatively saturated 1:2 ones containing unidentate ligands such as pyridine and its derivatives,$^{1)}$ pyridine *N*-oxide,$^{10)}$ aniline and its derivatives.$^{11)}$ Single crystal X-ray studies revealed that these adducts are of *cis*- or *trans*-octahedral configuration. Bidentate neutral ligands also add to metal(II) β-diketonates to form *cis*-octahedral 1:1 adducts more stable than those of unidentate donors owing to the chelate effect.$^{12-14)}$ Even bis(acetylacetonato)copper(II) was found to form a six-coordinate adduct with ethylenediamine, which is stable under dry conditions.$^{14)}$ However, only copper(II) complexes have been referred to in these reports, and the structures as well as the properties of the adducts of other metal(II) β-diketonates should be investigated in some detail.

The present paper describes the mixed ligand complexes of the types: M(hfa)$_2$(py)$_2$, M(hfa)$_2$phen,$^{15)}$ and M(hfa)$_2$bpy, where M=Co(II), Ni(II), Cu(II), and Zn(II); Hhfa=hexafluoroacetylacetone; py=pyridine; phen=1,10-phenanthroline; bpy=2,2′-bipyridine. The phen and bpy adducts are expected to be most stable because of both the presence of CF$_3$- groups and the chelate effect by the bidentate neutral ligands. Infrared spectroscopy was mainly used for estimation of the structures and the strength of metal-ligand bonds. Thus far few reports have been published on the infrared spectra of base adducts, while those of metal β-diketonate complexes have been studied extensively. The mass spectra of the phen and bpy adducts were also investigated in order to obtain information on the stabilities of the adducts against electron impact.

Experimental

Preparation of Complexes. M(hfa)$_2$$^{16)}$: A KOH solution was neutralized with Hhfa. This solution was mixed with a metal(II) acetate solution in a 2:1 molar ratio. The precipitate immediately formed was filtered, dried over P$_2$O$_5$, and recrystallized from methanol. M(hfa)$_2$(py)$_2$: M(hfa)$_2$ was dissolved in hot neat pyridine, and crystals formed on slow cooling were filtered and dried carefully. M(hfa)$_2$phen and M(hfa)$_2$bpy: Methanol solutions of M(hfa)$_2$ and each nitrogenous base were mixed in a 1:1 molar ratio. After standing overnight, crystallized adduct was filtered and dried over P$_2$O$_5$. The analytical data for isolated complexes are given in Table 1.

Table 1. Analytical data for the isolated adducts

Compound	C(%)		H(%)		N(%)	
	Calcd	Found	Calcd	Found	Calcd	Found
Co(hfa)$_2$(py)$_2$	38.06	38.46	1.92	2.11	4.44	5.00
Ni(hfa)$_2$(py)$_2$	38.06	39.47	1.92	1.87	4.44	4.14
Cu(hfa)$_2$(py)$_2$	37.78	37.72	1.90	1.88	4.41	4.40
Zn(hfa)$_2$(py)$_2$	37.67	38.52	1.90	2.16	4.39	4.98
Co(hfa)$_2$phen	40.46	41.00	1.54	1.60	4.29	4.49
Ni(hfa)$_2$phen	40.46	41.56	1.54	1.66	4.29	4.63
Cu(hfa)$_2$phen	40.17	40.21	1.53	1.56	4.26	4.42
Zn(hfa)$_2$phen	40.06	41.37	1.53	1.64	4.25	4.65
Co(hfa)$_2$bpy	38.18	38.62	1.61	1.68	4.45	4.57
Ni(hfa)$_2$bpy	38.19	38.46	1.61	1.64	4.45	4.65
Cu(hfa)$_2$bpy	37.90	37.78	1.59	1.60	4.42	4.45
Zn(hfa)$_2$bpy	37.73	37.55	1.59	1.58	4.40	4.42

Apparatus and Measurements. Infrared spectra were measured using a Hitachi EPI-G3 (4000—700 cm^{-1}) and a Nippon Bunko IR-F (700—200 cm^{-1}) infrared spectrophotometer. Samples were in the form of Nujol mulls between sodium chloride (4000—700 cm^{-1}) or KRS-5 (700—200 cm^{-1}) plates. X-Ray powder diffraction patterns were obtained using a Rigaku Denki 4051-5055 X-ray diffractometer with Cu*Kα* radiation. Mass spectra were obtained on a Nihon Denshi JMS-07 mass spectrometer under the following conditions: ion source temperature 300 °C, ionization voltage 30 V, ion accelerating voltage 3 kV, ionization current 300 μA.

Results and Discussion

The infrared spectra of the adducts exhibited no band due to free carbonyl group or free nitrogenous base, which shows these complexes to be six-coordinate. Of course, the only reasonable structure for the phen or bpy adduct is *cis*-octahedral one, whereas either *cis* or *trans* isomer may be present in the case of the pyridine adduct.

Strong absorption bands due to the C–O stretching modes[1] were observedaround 1650 cm^{-1}. Published works have often referred to C–O stretching vibrations for the purpose of obtaining indirect information on the metal–oxygen bonds. However, it seems to us that no clear correlation exists between the perturbed C–O stretching vibration and the strength of M–O bond.[18,19]

Table 2. Metal-sensitive bands of M(hfa)$_2$ (py)$_2$, M(hfa)$_2$phen, and M(hfa)$_2$bpy (cm^{-1})

Co(hfa)$_2$ (py)$_2$	Ni(hfa)$_2$ (py)$_2$	Cu(hfa)$_2$ (py)$_2$	Zn(hfa)$_2$ (py)$_2$	Assignment
667 s	673 s	667 s	665 s	ν(M–O)$_1$
635m	636m	648 sh	637m	py (6a)
585 s	588 s	583 s,br	584 s	ν(M–O)$_2$
428m 422 sh	436m	443m 434m	426m 419.5 sh	py (16b)
384w	404w	376m	372.5m	ν(M–O)$_3$
341w	345w	333w	340w	ν(M–O)$_4$
315m	326m	314.5m	311m	ν(M–O)$_5$
255 sh	250 m,br	264m	255w	
236.5m		240 sh	211m	

Co(hfa)$_2$ phen	Ni(hfa)$_2$ phen	Cu(hfa)$_2$ phen	Zn(hfa)$_2$ phen	Assignment
667.5 s	670 s	665 s	663 s	ν(M–O)$_1$
646w	648 sh	652 sh	647 sh	phen
585 s	586 s,br	585 s 578 sh	583 s,br	ν(M–O)$_2$
427m	429m	433.5m	427m	phen
387w	393m	379w	374w	ν(M–O)$_3$
343w	346.5w	337w	342.5w	ν(M–O)$_4$
314w	317m	a	308w	ν(M–O)$_5$
291m	298m	308m	290m	phen
252m	258 m,br	265 m,br	252w	
240 sh	244 sh,br	235w	240w	

Co(hfa)$_2$ bpy	Ni(hfa)$_2$ bpy	Cu(hfa)$_2$ bpy	Zn(hfa)$_2$ bpy	Assignment
665 s	669.5 s	665 s	664 s	ν(M–O)$_1$
637w	640w	643w	636w	bpy
585 s	587 s	587 s 579 sh	584.5 s	ν(M–O)$_2$
413m	415m	416m	412m	bpy
385w	392.5w	380w	372.5w	ν(M–O)$_3$
343w	347w	337w	343w	ν(M–O)$_4$
316.5w	319.5w	312w	313w	ν(M–O)$_5$
278m	289m	294.5m		
250w	259m	261w	250m	

a) Overlapped by the neighboring band.

Table 2 summarizes the metal-sensitive bands of the adducts in the far-infrared region. Above 700 cm^{-1}, almost all the bands observed are associated with vibrational modes of the ligands. The spectra in this region are very similar, and each band exhibited almost no sensitivity to a metal. Therefore, no further effort was devoted to examining the spectra above 700 cm^{-1}.

The pyridine ring vibrations located at 405 cm^{-1} (vibration 16b, out-of-plane ring deformation) and at 604 cm^{-1} (vibration 6a, in-plane ring deformation) in free pyridine are known to suffer marked shifts toward higher frequencies upon coordination to a metal.[20] In the pyridine adducts, the frequencies of the above bands showed the following order: cobalt(II)<nickel(II)<copper(II)>zinc(II). This is the same order as that reported in the literatures,[21,22] in which it is suggested that in a series of isostructural complexes, the frequencies of these two bands increase with a decrease in ionic radius of a metal. This conclusion is doubtful because the effective ionic radii of six-coordinate cobalt(II), nickel(II), copper(II), and zinc(II) ions are reported to be 0.73, 0.77, 0.81, and 0.83 Å, respectively.[23] Doublings of the 405 cm^{-1} band took place except for the case of the nickel(II) adduct, which is ascribed to the result of some interaction between different pyridine molecules.[22]

The assignments of phen and bpy vibrations in Table 2 are based on the work of Huchinson *et al.*[24] It is worth noting that the observed frequencies of the bidentate ligands vibrations showed the same order with the case of the pyridine ones. The frequencies of these vibrations may be reflection of some factors such as metal–nitrogen bond length, the strength of back-bonding, the polarizing power of metal ion.[21]

Metal-oxygen (M–O) stretching bands were assigned on the basis of the metal ion substitution technique applied extensively by Thornton *et al.*[25–27] It is generally recognized that in a series of isostructural complexes, substitution of a metal ion by another leads to a remarkable shift in a metal-ligand stretching frequency. The infrared spectra of the adducts showed five metal-sensitive bands in common in the 700—300 cm^{-1} region. These bands are considered to contain M–O stretching character to a varying degree bacause of the strong coupling between various vibrational modes. The bands observed at 405—370 cm^{-1} can be assigned to the least-coupled M–O stretching modes because they exhibit the maximum sensitivity to the metal ions. Since the transition metal(II) ions in the present study have similar masses, the variation in M–O stretching frequency may be considered to reflect the variation in the force constant of the M–O bond to a first approximation.

The M–O stretching frequencies of the adducts were found to decrease as follows: nickel(II)>cobalt(II)>copper(II)>zinc(II), which is inconsistent with the so-called Irving-Williams stability order: cobalt(II)<nickel(II)<copper(II)>zinc(II). The M–O stretching frequencies of metal(II) β-diketonates have been shown to follow this natural rule.[25,28] Hancock and Thornton[17] assigned the band at 427 cm^{-1} of Cu(hfa)$_2$·H$_2$O to the copper-oxygen (Cu–O) stretching vibration, and the present study shows that M–O stretching frequencies of Ni(hfa)$_2$ and Zn(hfa)$_2$ are 404 and 385 cm^{-1}, respectively.

The above results revealed that adduct formation causes a low-frequency shift of the M–O stretching band except for the case of Ni(hfa)$_2$(py)$_2$. The magnitudes of shifts were 11—13 cm^{-1} for nickel(II), zinc(II) complexes and about 50 cm^{-1} for copper(II), respectively. The shifts in the cobalt(II) complexes would be as large as those in the nickel(II) and zinc(II) complexes.[29)]

These shifts can generally be explained in terms of the electrostatic repulsion between a neutral base and hfa. Anhydrous M(hfa)$_2$ are estimated to have a polynuclear octahedral geometry [M=Co(II), Ni(II), and Zn(II)] like acetylacetonate analogues of these metals.[1)] A considerable "crowding" of donor ligands exists in the six-coordinate complex of a first-row transition metal(II). Thus, the coordination of more basic nitrogenous base in place of bridging oxygen atoms leads to the increased repulsion toward hfa, with the result that M–O distances are slightly lengthened. This interaction may be assumed to be caused by induced charges through the d orbital of the metal(II) ion.[7)] Similar low-frequency shifts have been reported for bis(nitrogenous base) adducts of nickel(II) acetylacetonate[11)] and metal(II) thenoyltrifluoroacetonates.[29)] The Lewis acidity of a metal(II) β-diketonate is enhanced by the introduction of an electron-withdrawing substituent to the β-diketone ligand. This fact may be ascribable to the reduction in the repulsion described above owing to a decrease in the electron density around the central metal(II) ion.

In the case of the copper(II) complexes, exceptionally large shifts of about 50 cm^{-1} were observed, which cannot be ascribed only to the repulsion effect. There are two possible interpretations for these results. One is that the coordination number of copper(II) changes from five in Cu(hfa)$_2$·H$_2$O to six in the adducts. Increased coordination number generally causes a considerable low-frequency shift of metal-ligand stretching bands.[26)] However, the shift as much as 50 cm^{-1} seems to be too large even if the change in coordination number is taken into consideration.

A more plausible explanation can be offered by considering a structure that has Jahn-Teller distortion arising from the d^9 electron configuration of copper(II) ion.[29)] The *cis*-equatorial structure of Cu(hfa)$_2$(py)$_2$ and Cu(hfa)$_2$bpy has been established by single crystal X-ray studies.[7,12)] In view of the fact that the Cu–O stretching bands of the three copper(II) adducts appeared at approximately the same frequency, Cu(hfa)$_2$phen is thought to have a *cis*-equatorial structure as well (Fig. 1). The coordinating ability of phen is evidently higher than that of hfa which is the least basic in a series of β-diketonate ions.[30)] The significant back-donation as well as the chelate effect will stabilize the bonds between copper(II) and phen. It is, therefore, reasonable to conclude that phen occupies the equatorial sites, forming a most stable chelate ring with copper(II) ion.

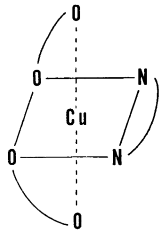

Fig. 1. The estimated structure of Cu(hfa)$_2$phen.

In each copper(II) adduct, one oxygen atom in hfa occupies the equatorial position. On the other hand, the other oxygen coordinates along the axial direction, which results in a longer and weaker Cu–O bond than the former. The observed Cu–O stretching bands of the adducts are considered to exhibit a character intermediate between the long and the short Cu–O bonds because of the vibrational coupling.[31)] Consequently, the Cu–O stretching band of the copper(II) adduct appears at much lower frequency than that of Cu(hfa)$_2$·H$_2$O in which the four equatorial sites are estimated to be occupied by hfa.

It should be noted that the nickel-oxygen (Ni–O) stretching band of Ni(hfa)$_2$(py)$_2$ showed a negligible low-frequency shift on adduct formation. This fact seems to exclude the possibility of Ni(hfa)$_2$(py)$_2$ having the *cis* arrangement of pyridine molecules because the Ni–O steretching bands of Ni(hfa)$_2$phen and Ni(hfa)$_2$bpy, for which only a *cis*-octahedral structure is assumed. shifted toward the lower frequencies to the same extent as the other phen and bpy adducts. Single crystal X-ray studies[7)] revealed that bis pyridine adducts of Cu(hfa)$_2$ and Zn(hfa)$_2$ are of *cis*-octahedral geometry, Cu(hfa)$_2$(py)$_2$: monoclinic, P2$_1$/c; Zn(hfa)$_2$(py)$_2$: monoclinic, C2/c. Figure 2 gives the X-ray powder patterns of the pyridine adducts. Since Co(hfa)$_2$(py)$_2$ was isomorphous with Zn(hfa)$_2$(py)$_2$, a *cis* structure is also implied. On the other hand, Ni(hfa)$_2$(py)$_2$ did not show any feature of isomorphism with the *cis* Cu(hfa)$_2$(py)$_2$ and Zn(hfa)$_2$(py)$_2$ species. As Horrocks *et al.* suggested,[32)] there is little energy difference between *cis* and *trans* forms of such adducts, and a *trans* isomer may well be present in the crystalline state. However,

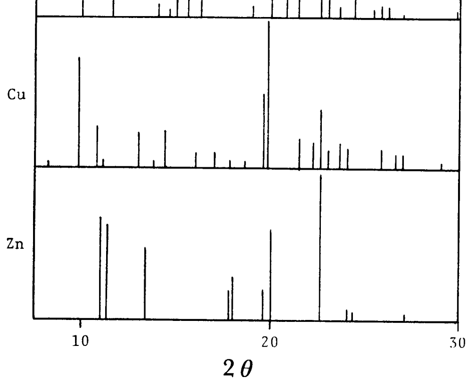

Fig. 2. X-ray powder patterns of M(hfa)$_2$(py)$_2$.

it is impossible at present to make a conclusive decision regarding a *trans* arrangement in Ni(hfa)$_2$(py)$_2$.

It has been established that the increased donor capacity of a nitrogenous base for a metal ion leads to a reduction in M–O stretching frequency.[11,29] However, the pyridine, phen, and bpy complexes showed no marked difference in M–O stretching frequencies. Incorporation of strongly electron-withdrawing CF$_3$-groups into β-diketone must result in weaker and longer M–O bonds. Thus, the interaction between hfa and a neutral ligand may be relatively weak, and the strength of M–O bonds is hardly affected by slight differences in the basicities of the three nitrogenous bases[33] (pK_a: py 5.22, phen 4.86, bpy 4.35).

The metal–nitrogen (M–N) stretching vibrations are expected to lie below 300 cm^{-1}. However, the assignment of metal pyridine stretching band has been subject to some confusion. In the infrared spectrum of Ni(acac)$_2$(py)$_2$ (Hacac=acetylacetone), the 249 cm^{-1} band was assigned to the nickel-nitrogen (Ni–N) stretching mode by Nakamoto *et al.*,[34] whereas Haigh *et al.*[11] indicated the absence of any band due to Ni–N stretching mode in the region above 200 cm^{-1}. To our knowledge, no reports have been published on the assignment of the M–N stretching vibration of six-coordinate mono phen or bpy complex. Therefore, we did not make any effort to assign the M–N stretching bands of the adducts although a few netal-sensitive bands were observed between 300 and 200 cm^{-1}.

The mass spectrometry of M(hfa)$_2$phen and M(hfa)$_2$bpy was investigated in order to examine the fragmentation of the adducts under electron impact. Though the mass spectra of metal β-diketonates have been studied extensively,[35–37] those of base adducts are still unknown. Table 3 lists the relative intensities of the main fragment peaks. The spectra in the *m*/*e* region greater than 500 where parent peaks might appear could not be measured because of the limitation of the apparatus used.

Table 3. Relative intensities of metal-containing ions in the mass spectra of M(hfa)$_2$phen and M(hfa)$_2$bpy L: hfa, B: phen or bpy

Ion	M(hfa)$_2$phen				M(hfa)$_2$bpy		
	Co	^{58}Ni	^{63}Cu	^{64}Zn	Co	^{58}Ni	^{64}Zn
LMB$^+$	100	100	100	100	100	100	74
(L$_2$M–CF$_3$)$^+$			37	45	8		100
(L$_2$M–2CF$_3$)$^+$			15				
F-MB$^+$	34	50		45	38	21	22
MB$^+$			78				
(LM–CF$_3$)$^+$			77				

The previous study[38] on the thermal stability of the synergistic adducts of copper(II) β-diketonates has demonstrated that a unidentate pyridine base is readily released during thermal decomposition process. The thermal stability of phen or bpy adduct is expected to be enhanced far more exceedingly than that of pyridine adduct because of the chelate effect. In fact, no thermal decomposition of the adducts was observed during the mass spectral measurement except for the case of Cu(hfa)$_2$bpy.

It became evident that Cu(hfa)$_2$bpy decomposed into Cu(hfa)$_2$ and bpy prior to electron impact since the mass spectrum of Cu(hfa)$_2$bpy corresponded to just a superposition of that of Cu(hfa)$_2$ and bpy. The observed difference in the thermal stability between Cu(hfa)$_2$phen and Cu(hfa)$_2$bpy is mainly ascribable to the decreased rigidity of bpy molecule in comparison with that of phen. As the result of the above reaction, bpy molecule comes to rotate freely around the C–C bond between the two aromatic rings, which contributes positively to the entropy term of the free energy change in the decomposition reaction. A more reduced d$_\pi$–p$_\pi$ interaction in the adduct of bpy having a shorter conjugated system may also play an important part.

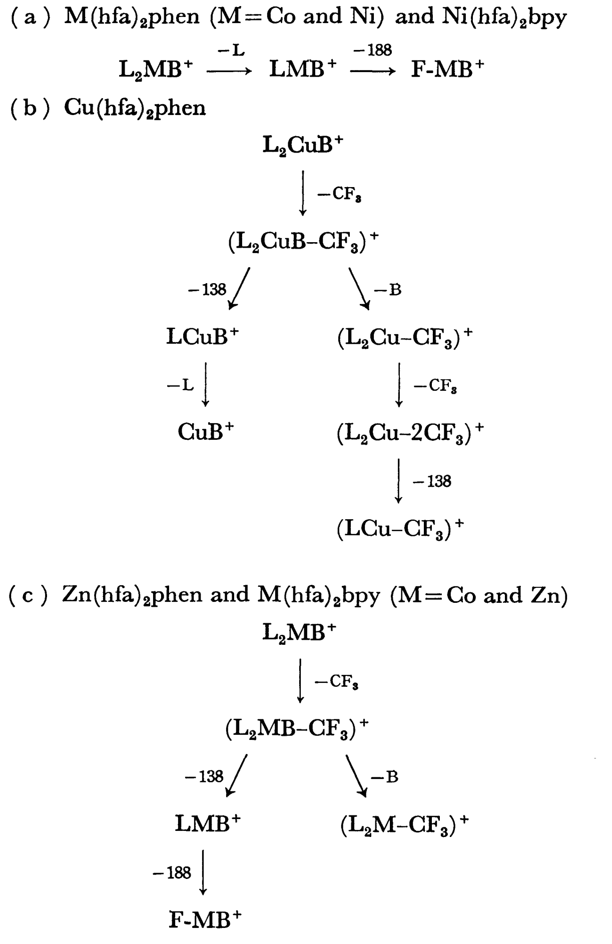

Chart 1. Mass fragmentations of M(hfa)$_2$phen and M(hfa)$_2$bpy.
L: hfa, B: phen or bpy

The fragmentation sequences assumed with regard to metalcontaining ions are shown in Chart 1. The fragmentation of L$_2$MB$^+$ to LMB$^+$ may occur *via* initial loss of CF$_3$ and subsequent loss of CF$_3$COCHCO (mass 138). The nitrogenous beses in the group (a) adducts are bound more firmly to metal ions than those belonging to groups (b) and (c). In the latter complexes, the fragment ions containing no nitrogenous base, (L$_2$M–CF$_3$)$^+$ were detected. It is reported that elimination of CF_2 occurs with migration of a fluorine atom to the metal in $Zn(hfa)_2$ and $Al(hfa)_3$.[36] The whole residual ligand $CF_3COCHCOCF_2$ (mass 188) was lost in the corresponding process of the phen and bpy adducts.

After loss of one hfa radical, Cu(hfa)phen$^+$ undergoes quite a unique fragmentation, *i.e.*, Cu(hfa)phen$^+ \longrightarrow$ Cu-phen$^+ + \cdot$hfa. It is interesting to note that Cu-phen$^+$ formally involves Cu(I). Of the present four metals, only copper is relatively stable in the univalent state. A decrease in valency of a metal generally leads to increased covalent character of the metal-ligand bonds.[36] Thus, the copper-nitrogen bonds in Cu-phen$^+$ are fairly stabilized through the strong copper(I)-to-ligand back-donation.

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