Notes

Infrared Spectra of Metal Chelate Compounds of Hexafluoroacetylacetone

By Melvin L. Morris, Ross W. Moshier,
and Robert E. Sievers

The hexafluoroacetylacetone (HFA; $CF_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CF_3$) complexes of Cu(II), Ni(II), Co(II), Nd(III), Rh(III), Fe(III), and Cr(III) have been reported in the earlier literature.[1-5] During the course of this

recently: $Cu(HFA)_2 \cdot H_2O$,[6] m.p. 126–128°; $Zn(HFA)_2 \cdot 2H_2O$, m.p. 153–154°; $Ni(HFA)_2 \cdot 2H_2O$, m.p. 207–208°; $Co(HFA)_2 \cdot 2H_2O$, m.p. 172–174°; $Mn(HFA)_2 \cdot 2H_2O$, m.p. 155–156°; $Fe(HFA)_2 \cdot 2H_2O$, decomposes on heating; $Rh(HFA)_3$, m.p. 114–115°; $Fe(HFA)_3$, m.p. 49°; $Cr(HFA)_3$, m.p. 84–85°; $Al(HFA)_3$, m.p. 73–74°; $Nd(HFA)_3 \cdot H_2O$, melts with gas evolution at 115–121°; $Th(HFA)_4$, m.p. 121–122°; and $Zr(HFA)_4$, m.p. 152–154°.

Two general methods were used in the preparation of these compounds. The first method involved the addition of an aqueous solution of the neutralized ligand to an aqueous solution of the cation. In the second method the ligand was added directly to a suspension of the anhydrous metal chloride in carbon tetrachloride. In this method, hydrogen chloride is evolved and the addition of a base is unnecessary. Since the methods of preparation for several of these compounds are

TABLE I
INFRARED SPECTRA OF HFA COMPLEXES

Metal ion	OH str.	C=O str.[c]	C=C str.[c]	C=O str. CH bend			CC str. CF$_3$ str.	CF$_3$ str.		CH in plane bend		CH out of plane bend C–CF$_3$ str.	C–CF$_3$ str.	
Rh(III)		1610 (s)	1628 (sh)	1560	1534	1426 / 1453	1348	1258	1218	1155	1108	823 / 812	752	712 / 706
Cr(III)		1612 (s)	1639 (sh)	1563	1546	1422	1356	1258	1221	1174	1112	815 / 828	748 / 738	678
Fe(III)[a]		1613 (s)	1641 (m)			1438 / 1412		1252	1222	1173	1114			663
Al(III)		1654 (s)	1636 (sh)	1578	1552	1483 / 1452	1370	1262	1222	1162 / 1150	1048 / 1122	816	748 / 774	672
Th(IV)		1652 (s)	1622 (sh)	1577	1543	1500	1353	1262	1228	1152	1106	808	742	660
Ni(II)	3432	1649 (s)	1615 (w)	1565	1536	1468	1350 / 1388	1258	1224	1150	1098	808	744	674
Co(II)	3370	1648 (s)	1618 (sh)	1564	1536	1483	1384 / 1350	1258	1228	1148	1098	808	742 / 772	668
Nd(III)	3360	1657 (s)	1618 (sh)	1568	1542	1498 / 1418	1348	1258	1227	1153	1101	808	772 / 742	662
Zn(II)	3440	1650 (s)	1614 (w)	1568	1538	1460	1378	1260	1219	1148	1090	808	772 / 722	669
Mn(II)	3438	1650 (s)	1613 (sh)	1562	1538	1493 / 1463	1344	1258	1214	1152	1088	802	768 / 743	665
Fe(II)[b]	3370	1640 (s)	1613 (s)	1568	1538		1352	1260	1224	1148	1102	804	742	663
Zr(IV)		1650 (s)	1627 (s)	1567	1542	1476	1362	1254	1222	1156	1118	832 / 812	744	659
Cu(II)[b]	3590	1652 (s)	1620 (m)	1568	1541		1378	1258	1211	1148	1108	806	746 / 718	678

[a] CCl$_4$. [b] Nujol mull, the other compounds were determined in KBr and dry Nujol. [c] w, weak; m, medium; s, strong; sh, shoulder.

investigation the synthetic methods have been refined and the melting points determined for these compounds and six other compounds which were synthesized

modifications of existing procedures they are not reported here.

The infrared spectra of the Cu(II) and Ni(II) complexes have been determined and interpreted.[2] In this study the infrared spectra of thirteen metal complexes have been determined and are given in Table I. In general the spectra of these compounds are quite similar. The spectra of the divalent complexes show a

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(6) Melting points are uncorrected.

peak in the 3350 to 3600 cm.$^{-1}$ region, which is assigned to the OH stretching frequency of coördinated water. This observation and the analytical data indicate that these complexes are dihydrates with the exception of the Cu(II) complex, which is a monohydrate. Attempts to dehydrate the Fe(II), Ni(II), Zn(II), Co(II), and Mn(II) complexes by sublimation were unsuccessful. The most intense band in the 1600 cm.$^{-1}$ region has been assigned to the carbonyl stretching frequency.[7] When the position of this band is compared for the different metal complexes, an interesting correlation is observed.

Sievers and Bailar[8] have shown for metal polyaminocarboxylate chelates that the position of the carbonyl stretching frequency is influenced by the charge to radius ratio q/r of the metal ion. It was found that the carbonyl stretching frequency of the carboxyl groups bonded to metals with q/r ratios of more than 3.6 occurred between 1625 and 1650 cm.$^{-1}$, and for those less than 3.6, at 1590 to 1615 cm.$^{-1}$.

In hexafluoroacetylacetonato complexes, in contrast with the complexes of carboxylic acids, coördination occurs through the oxygen of the carbonyl group, and the position of the carbonyl stretching frequency is shifted in opposite directions for these two classes of compounds. In metal–HFA complexes, it is expected that the band position of carbonyl groups attached to metals of high q/r ratios will be lower than those bonded to metals of low q/r ratios. The metals with high q/r ratios bond more strongly with the oxygen, thus reducing the double bond character of the carbon–oxygen bond.

Table I shows that the carbonyl stretching frequencies of the divalent metal ions and Nd(III), which have q/r values ranging from 2.2 to 2.6, appear at approximately 1650 cm.$^{-1}$; those of the trivalent metal ions Rh, Cr, and Fe, which have q/r values from 4.4 to 4.6, appear at 1610, 1612, and 1613 cm.$^{-1}$. If the charge to size ratio criteria is used, it is found that only for Al(III) and Zr(IV), whose q/r ratios are high, are results found contrary to those predicted.

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Contribution from the Chemistry Department,
University of Kansas City,
Kansas City, Missouri

Chloride and Bromide Complexes of Nickel(II) in Aqueous Solution[1]

By D. A. Netzel and H. A. Droll

We wish to report on the small but significant changes in the visible absorption spectra of Ni(ClO$_4$)$_2$ solutions

(1) Abstracted in part from the M.S. thesis of D. A. Netzel.

that contain relatively large concentrations of either chloride or bromide ions. Ion-exchange[2-4] and spectrophotometric studies indicate the presence of only either NiCl$^+$ or NiBr$^+$ in highly concentrated hydrohalic acid solutions of nickel(II). Recently, Lister and co-workers[5,6] failed to observe any spectral change in the range 240–900 mμ for chloride- and bromide-containing solutions of Ni(ClO$_4$)$_2$ at halide concentrations up to 0.12 M. However, we have observed changes of up to 18% in the optical density of 0.0447 M Ni(ClO$_4$)$_2$ solutions whose halide concentrations exceed 0.12 M (Table I). Unfortunately, these spectral changes occur in only an extremely narrow range of wave lengths near the maximum absorption at 400 mμ. We assume that a 1:1 complex is present which is responsible for the absorption shift. Since the absorption shift is small, the molar extinction coefficients ϵ_0 and ϵ_1 for Ni(aq)$^{2+}$ and NiX$^+$ (X = Cl, Br), respectively, are nearly equal. The equation

$$\bar{\epsilon}[\text{X}^-]/(\bar{\epsilon} - \epsilon_0) = \epsilon_1[\text{X}^-]/(\bar{\epsilon} - \epsilon_0) - 1/K$$

which relates the average molar extinction per nickel (optical density/total nickel concentration) to the stability constant, K, for the 1:1 complex, is derived from Beer's law, the stability constant expression for NiX$^+$, and the assumption that the equilibrium halide concentration equals the total halide ion concentration. This equation is the slope–intercept form of a straight line whose slope is the molar extinction coefficient for NiX$^+$ (ϵ_1) and whose intercept is the reciprocal of the stability constant. Table I includes values of the functions $\bar{\epsilon}[\text{X}^-]/(\bar{\epsilon} - \epsilon_0)$ and $[\text{X}^-]/(\bar{\epsilon} - \epsilon_0)$ calculated from the optical density values. An implied accuracy of 2% in the optical density measurements leads to an approximate accuracy of about 20% for these functions. These functions when plotted yield a straight line.

Application of the method of average points enables us to estimate values for the stability constants, valid at an ionic strength of 5.7 M: $K = 0.3 \pm 0.1$ for Ni^{2+} + Cl$^-$ $\rightleftarrows$ NiCl$^+$ and $K = 0.5 \pm 0.2$ for Ni^{2+} + Br$^-$ $\rightleftarrows$ NiBr$^+$. Similarly, the molar extinction coefficients for NiCl$^+$ and NiBr$^+$ for both wave lengths given in Table I are evaluated to be 6 $\pm$ 1 l. mole^{-1} cm.$^{-1}$. The molar extinction coefficients for Ni(aq)$^{2+}$ at 395 and 400 μ are 5.0 $\pm$ 0.1 and 4.7 $\pm$ 0.1 l. mole^{-1} cm.$^{-1}$, respectively.

Experimental

Reagents.—Reagent grade Ni(ClO$_4$)$_2$·6H$_2$O (G. Frederick Smith Co., Columbus, Ohio) was used without further purification to make the standard nickel solution about 0.5 M in nickel-(II) and 1 M in perchloric acid. Aliquot samples were taken and the amount of nickel was determined by precipitation with dimethylglyoxime. The final nickel solution contained 0.491 M Ni^{2+} and 1.987 M ClO$_4$$^-$.

A series of mixed 6 M HX–6 M HClO$_4$ solutions was obtained

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