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pH Dependence of Surface Species Formed by the Adsorption of Cobalt and Nickel Glycinates on Alumina: A Tunneling Spectroscopy Study

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The vibrational spectra of a few nickel and cobalt glycinates as adsorbates on alumina are studied by tunneling spectroscopy. The pH dependence of the spectra obtained from alumina which had been exposed to solutions of 10^{-3} mol/L of the complexes or parent glycine are reported. In the case of glycine adsorption, the results obtained are in good agreement with those reported by others, but a modified interpretation is presented. It is demonstrated that cobalt(III) and nickel(II) glycine complexes preferentially adsorb on alumina from dilute solutions of pH in the range 4–9. It is further shown that the dominant surface complex in both cases is one in which glycine acts as bidentate glycinate. The data presented are insufficient to determine whether the complexes are di- or monoglycinates. The free spectral range exhibited by tunneling spectroscopy is shown to provide more information than infrared spectroscopy as applied to adsorbed metal glycine complexes. The present results are discussed relative to those obtained from solid, solution, and surface state complexes of the type studied.

Introduction

Inelastic electron tunneling spectroscopy (IETS) is a vibrational spectroscopy which has been extensively used to study the adsorption of organic molecules on alumina.[2,3] Recently, its usage has been extended to the study of the adsorption of iron cyanide complexes[4,5] and zirconium tetraborohydride on alumina.[6] The two principal advantages of IETS over more conventional techniques are (a) a nearly perfect window from 300 to above 4000 cm^{-1} in the spectrum obtained from the alumina support (the only strong band is at 920 cm^{-1} and is about 90 cm^{-1} wide) and (b) the possibility of observing bands that are Raman and/or IR allowed as well as transitions which are forbidden in photon spectroscopies. These advantages make it imperative that the applicability of IETS to inorganic spectroscopy be fully explored. This work will consider the adsorption of metal glycine complexes on alumina.

Groenewegen and Sachtler[7,8] have studied the adsorption of amino acids in the vapor phase on silica-supported nickel (Ni/SiO_2) and SiO_2 by infrared spectroscopy. Although the region below 1200 cm^{-1} was dominated by substrate adsorption, the CO, NH, and CH stretching region allowed a partial assignment of the surface species to be made. The authors concluded that glycine was present on the surface in anionic form and that binding to Ni occurred through both Ni–N and Ni–O bonds. They were unable to determine if the adsorption process produced a mono- or diglycine complex. An additional observation was that glycine did not appear to adsorb on the support. Yoneda et al.[9] and Lederer and Battiloti[10] have studied the relative strengths of adsorption of a series of Co(III) complexes on alumina. While all the complexes studied adsorbed to some extent, anionic complexes adsorbed most strongly. Unfortunately, Yoneda et al. did not report the pH dependence of the adsorption process, nor did they investigate the possibilities of reductive or dissociative adsorption.

The major objectives of this paper were to determine whether IETS is an appropriate tool for studying metal glycine complexes, to ascertain the effects of solution pH on the surface species obtained, and to contrast the IETS intensities with those obtained in IR and Raman experiments. The implied questions above, regarding the nature and orientation of the surface complex, are especially difficult ones for the metal–glycine systems studied.

Glycine in aqueous solution can exist in any of three forms, the relative amounts of each depending on solution pH.[11] The cationic form is dominant below about pH 3, while a dipolar anion is the major component between pH 3 and 9.[12] Above pH 10, the anionic form is the major component. These three forms have been extensively studied by Raman spectroscopy.[11,13] $ML_m{}^{n+}$ complexes, where L = glycine, also have several principal stoichiometries which depend on glycine concentration and pH.[12,14,15] Generally, one expects that m should increase with increasing pH and glycine concentration in water solution. The regions of stability in solution, however, may not correspond to those of the adsorbed species. Further, adsorption may be accompanied by geometrical isomerization in addition to the above chemical modifications. In the case of adsorption from a solution which is formally $Ni(gly)_2$ (gly = glycine), one must distinguish the various forms of glycine complexed to the alumina support from those complexed to Ni and then proceed to identify whether the system is NiL^+, *cis*-NiL_2, or *trans*-NiL_2. In connection with the identification of the bands due to glycine on alumina, Simonsen and Coleman[16] have previously reported the IETS of glycine at intermediate pH and state that the spectrum is pH independent to about pH 10. We have repeated their measurements and will provide a modified interpretation.

Experimental Section

Instrumental. The details of the construction of the spectrometer used in these studies have been presented elsewhere.[5,17] All reported spectra were obtained at 4.0 K with a 2-mV modulation amplitude and 675-Hz modulation frequency. This corresponds to an instrumental line width of about 25 cm^{-1}. Although our spectrometer is capable of considerably better resolution, the intrinsic line width of the bands observed from the Ni and Co complexes studied was such

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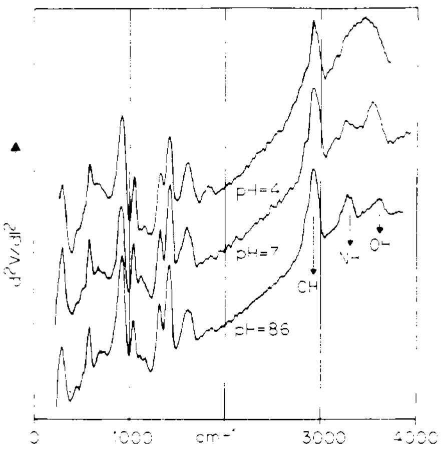

Figure 1. IETS of glycine adsorbed on alumina from water solution. Solution concentrations were approximately 0.001 mol/L, and the pH was adjusted to the values shown.

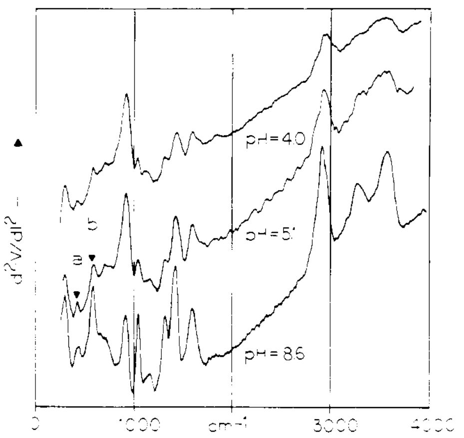

Figure 2. IETS of the nickel(II) glycinate surface complex as a function of pH.

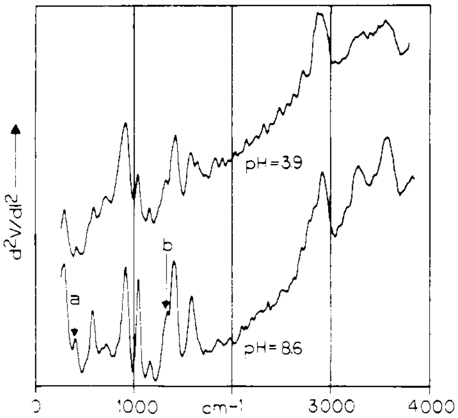

Figure 3. IETS of the cobalt(III) glycinate surface complex as a function of pH.

that little improvement in spectral structure was obtained by decreasing the instrumental line width by a factor of 2. In the case of the direct adsorption of glycine, the natural line width is significantly less than 25 cm^{-1} for a few of the bands. We have presented only the low-resolution (2 mV) spectra here in order that they may be fairly contrasted with those obtained from the metal complexes.

All of the data presented were from Al–Al$_2$O$_3$–X–Pb diodes, where X was the species of interest. The oxide was prepared by glow discharge in a 50 × 10^{-3} mmHg atmosphere of O$_2$. The nature of the oxide is dealt with in more detail in the Discussion, but it is primarily γ-alumina which is free from surface water, containing less than 0.1 OH$^-$/Å.[2] Solution doping was accomplished in one of two ways. Most of the spectra shown were obtained by placing about 2 mL of appropriate solution on the oxide surface and, after a period of about 1 min, spinning the substrate dry prior to Pb deposition. An alternate method was also used for obtaining the pH 5.1 Ni(gly)$_2$ spectrum in order to check surface equilibration with the solution pH. Freshly prepared Al–Al$_2$O$_3$ surfaces were immersed for a period of several minutes in a solution whose pH was previously adjusted (via HCl) to the pH of the dopant. The complex containing solution was then doped as above. No significant differences were observed. Compounds and complexes were doped from solutions freshly prepared from extensively purified solids. The pH of the solutions was adjusted by the addition of either NaOH or HCl. Typically, these solutions were 10^{-3} M. All solutions were prepared in water that was saturated with N$_2$ gas. Due to the nature of the doping process, quoted solutions concentrations are probably only qualitatively relevant.

Compounds. Glycine (gly) was obtained commercially. Ni(gly)$_2$·2H$_2$O,[18] Co(gly)$_2$,[19] KCo(gly)$_2$(NO$_2$)$_2$,[20] and Ni(gly)Cl[21] were prepared by standard methods. All complexes gave IR spectra which agreed with those in the literature.[19–22] Purified solids were stored in the dark.

Results

Figure 1 presents the tunneling spectra obtained from 10^{-3} mol/L solutions of glycine with pH adjusted to 8.6, 7.0, and 4.0. The pH 7 spectrum is identical with that reported by Simonsen and Coleman.[16] The most notable effects of the variation in pH occur in the regions of the spectra associated with NH and OH motion. At pH 8.6 the glycine NH stretching motions[27] occur at 3300 cm^{-1} and are well separated from the surface OH stretching bands[1] which maximize at 3630 cm^{-1}. At pH 7, the NH and OH stretching bands are beginning to fuse due to hydrogen bonding.[29] The band maximum of the surface OH motion has shifted down to 3545 cm^{-1}, and a low-frequency shoulder (3170 cm^{-1}) has developed in the NH stretching region. The full consequences of extensive hydrogen bonding are apparent in the pH 4 spectrum. One can no longer separate the bands due to NH and OH motion, although the shoulder at 3170 cm^{-1} is still apparent. NH-type motions are also encountered near 1130 and 700 cm^{-1},[23–25] although Krishnan[11] prefers to assign the Raman modes in the 700 cm^{-1} region to CO$_2$ scissoring motion. It is evident from Figure 1, that these regions of the tunneling spectrum are also sensitive to pH variation. Much less obvious is the growth of a shoulder at about 1650 cm^{-1} with decreasing pH. This band has also been assigned to NH-type motion.[16] The other low-frequency modes, primarily due to CCN- and CO-type motions, are essentially unaffected by the variation in pH. Peak positions for all the bands in the pH 8.6 spectrum of glycine are included in Table I.

Figure 2 displays the spectra obtained from 3 × 10^{-3} M solutions of Ni(gly)$_2$ with pH adjusted to 8.6, 5.1, and 4.0, respectively. There are several striking features about the pH dependence of the spectra displayed. As pH decreases, adsorption to the alumina surface, as measured by the strength of the tunneling spectrum, decreases. In all three spectra, there is a band, marked a, at 433 cm^{-1} which is not present in the glycine spectrum. With decreasing pH, the sharp band at 590 cm^{-1}, marked b, has decreased by about a factor of 2 relative to bands near 1500 cm^{-1}. The NH bands near 3300 cm^{-1} appear to shift to higher frequency with decreasing pH, but

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Table I. Tunneling and IR Spectral Peak Positions (cm^{-1}) for Some Glycine Complexes

IETS^c			IR^c		
gly	KCo(gly)$_2$(NO$_2$)$_2$	Ni(gly)$_2$	Ni(gly)$_2$^{b}	Ni(gly)Cl^a	assignments^b
	410	440	437	445	ν(NiN + NiO)
460					
526 sh	526 sh		518		CO$_2$ wag
587	588	590	596	595	CO$_2$ wag
			621	635	
681 vw		667 vw	676	680	ρ(NH$_2$)
746	727 b, w	724 vw	738	720	ρ(CO$_2$ + CH$_2$ + NH$_2$)
	Al$_2$O$_3$ band		790		
			916		
			950		
1056	1053	1047	1042	1032	ν(CN)
1118 w			1096	1093	NH$_2$ wag
1175 w	1166	1170	1185		ρ(CH$_2$) + ν(C–C)
1315	1294 sh	1320	1305	1300 sh	δ(NH$_2$ + CH$_2$)
	1341		1349	1340	[CH$_2$ + CO] wag
1420	1412	1420	1411	1410	ν(CO + CC)
			1439	1446 b	δ(CH$_2$)
1612	1590	1600	1590	1602	ν(CO$_2$)
1640 sh	1660 w sh		1610 sh		δ(NH$_2$)
2932	2920 b	2923	2937		ν_s(CH)
			2977	very	ν_a(CH)
		3200 ws	3190	broad	
3292	3285	3282	3273	bands	ν_{as}(NH)
			3328		ν_s(NH)

[a] Sheka, I. A.; Arsenin, K. I. *Ukr. Khim. Zh.* 1975, *41*, 563. See also this work. [b] Percy, G. C.; Stenton, H. S. *J. Chem. Soc., Dalton Trans.* 1976, 1466. [c] sh = shoulder; w = weak; v = very; b = broad.

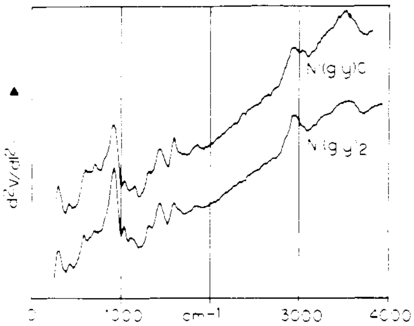

Figure 4. IETS of the surface complex formed by adsorption from solutions of the indicated complexes at pH 4.0.

this may be an artifact of the decrease in their signal strength relative to that of the OH modes. The reversal of the pH dependence of the strength of the OH stretching transition, relative to glycine, is also an interesting feature of these spectra. As shown in Table I, the pH 8.6 spectrum is very similar to that for solid Ni(gly)$_2$·2H$_2$O, especially since simple changes in the physical state of the bulk material are known to produce changes as large as 30 cm^{-1} in the observed bands.[26]

Figure 3 records the spectra obtained from diodes doped with 3 × 10^{-3} M KCo(gly)$_2$(NO$_2$)$_2$ at pH 8.6 and 3.9. Although the low-pH spectrum is noisy above 1600 cm^{-1}, it can be seen that with decreasing pH there are modifications in the intensities of the bands and that the expected broadening of the NH and OH stretching bands occurs. Both spectra show a new band, marked a, at about 410 cm^{-1}. Further, the well-defined band at about 1320 cm^{-1} which appears in the glycine and nickel glycine spectra has been replaced by a definite shoulder, marked b, near 1340 cm^{-1}. The sharp peak at 1166 cm^{-1} shows no tendency to shift or broaden with changing pH. The variation in relative intensities is complex; compare, for example, the intensities of the 588- and 1166-cm^{-1} bands at pH 8.6 and 4. Table I also contains the peak positions observed at pH 8.6 for the case of KCo(gly)$_2$(NO$_2$)$_2$ doping.

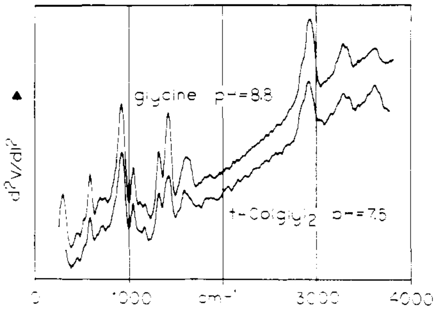

Figure 5. IETS of surface complexes formed by exposure of alumina to 10^{-3} mol/L solutions of glycine at pH 8.8 and *trans*-Co(gly)$_2$ at pH 7.5.

Figure 4 contrasts the spectrum obtained from a diode doped with Ni(gly)$_2$ with that obtained from an Ni(gly)Cl-doped diode, both solutions being held at pH 4. The spectra are basically indistinguishable within the limits of their respective signal to noise ratios. Further, a solution of Ni(gly)$_2$ to which a 50% excess of glycine was added produced identical results. Comparison with Figure 1 shows that these spectra are not simply due to adsorbed glycine. It would appear that (as yet unidentified) complexes of Ni and Co(III) with glycine preferentially adsorb to the alumina surface. This is not the case for *trans*-Co(gly)$_2$ adsorbed from solutions of 10^{-3}–10^{-2} M at pH 8, as is shown in Figure 5. The diodes doped with *trans*-Co(gly)$_2$ give spectra which are indistinguishable from those of glycine. No evidence for the cobalt(II) glycine surface complex was found.

Discussion

Glycine. Simonsen and Coleman[16] have reported the tunneling spectrum of glycine, and the pH 7 spectrum reported here is identical with theirs (see comments on resolution in the Experimental Section). Using Tsuboi's[23,24] assignments of the bands near 1600 and 1120 cm^{-1} as NH$_3$$^+$ motions and the close similarity of the 1600 cm^{-1} CO$_2$$^-$ band with that of the glycine zwitterion, they assigned the surface species as basically a zwitterion with the CO$_2$$^-$ group bonded to the surface. While it appears that this is correct for some of the

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sites, we doubt that the above species is the only contributor to the observed spectrum. As Groenewegen[7] and Bellamy[27] have pointed out, the zwitterionic form of glycine does not show bands in the normal NH region, but rather, one observes NH_3^+ stretching motions between 3030 and 3130 cm^{-1}. Bands near 3300 cm^{-1} are usually associated with metal glycine complexes in which there is metal–nitrogen bond formation.[26,27] Because of these observations, as well as the similarity of the glycine on alumina spectra to those of nickel and cobalt glycine complexes on alumina, we believe some fraction of the adsorbed glycine is present as the glycinate; that is, some of the surface glycines behave as bidentate ligands. The relative amounts of glycinate and zwitterionic glycine appear to vary with pH. At high pH, there is little indication of the NH_3^+ band near 3100 cm^{-1}, while the 3300-cm^{-1} band is quite strong. At pH 7, however, a well-defined shoulder is apparent near 3150 cm^{-1}. In our interpretation, aluminum glycinate is formed at high pH and is gradually replaced by zwitterionic glycine as the pH is lowered. This interpretation would also serve to explain the pronounced pH dependence of the weak bands between 1110 and 1180 cm^{-1}.

Ni(gly)$_2$ and Ni(gly)Cl. Figures 2 and 4 and Table I contain the tunneling data obtained from solutions of varying pH and containing about 10^{-3} mol/L of the species resulting from the solution of the indicated salts. Comparison of these data with the known spectra of the mono- and diglycine complexes of nickel[21,24,26,28] provides the strong indication that the observed tunneling spectra are due to a nickel glycine complex. Unfortunately, as evidenced by Table I, one cannot distinguish between the di or mono complex on the basis of comparison with infrared data alone. For example, one can clearly assign the band at 440 cm^{-1} as due to metal–nitrogen stretching; however, the inhomogenious broadening is such that it could well be 437 (Ni(gly)$_2$) or 445 cm^{-1} (Ni(gly)X). One is tempted to assign the surface nickel complex as the monoglycine on the basis of solution stability; the diglycine complex being least stable at low pH. This same argument, however, would lead one to deny the existence of a surface nickel glycine complex at pH 4.

It is also of interest to compare the tunneling spectra reported here with the IR spectra obtained by Groenewegen[7] from glycine adsorbed on Ni/SiO$_2$. The NH regions are nearly identical in position and contour, the resolution of his spectra are no better than those reported here, and the attenuation due to the support prevented measurements below 1300 cm^{-1}. While the above suggests that the tunneling method is superior to IR spectroscopy for studying adsorption on alumina, it should be born in mind that tunneling provides less flexibility in the choice of the physical state of the support. One is limited to either a hydrous alumina,[30] a mixture of amorphous alumina and γ-alumina[31] or γ-alumina.[32–34] In the case of solution-phase doping, our previous studies[4,5,17] have indicated that equilibration with aqueous solution dominates over the details of oxide growth for all cases except that of the hydrous alumina barrier. This is probably due to the formation of a thin layer of pseudoboehmite on contact with the aqueous solution.[35]

Co(gly)$_2^+$ and *trans*-Co(gly)$_2$. Solid KCo(gly)$_2$(NO$_2$)$_2$ is known to be solely the cis isomer; that is, the NO$_2$ ligands occupy adjacent vertices in a pseudooctahderal coordination scheme.[20] The absence of identificable NO_2^- bands in the tunneling spectrum, especially in the vicinity of 830 cm^{-1}, suggests that the NO_2^- ions are displaced from the coordination sphere of the adsorbed ion. The presence of a well-defined Co–N stretching band at 410 cm^{-1} indicates that at least one glycine is coordinated to cobalt.[20,22] The CO_2^- frequencies observed, as well as the Co–N band, argue for bidentate coordination.

The pH 8.6 spectrum is clearly different from any of the other spectra reported. As the solution pH is reduced to 4, there are definite changes in the spectrum observed. The very sharp CN stretching mode at 1053 cm^{-1} decreases in frequency by 11 cm^{-1}, and its intensity relative to the CH peak decreases dramatically. This same relative intensity decrease occurs for the band at 588 cm^{-1}. Also, the strong shoulder at 1341 cm^{-1} decreases in energy to 1325 cm^{-1}. The Co–N band appears to move up in frequency with decreasing pH, although this may be an artifact of the difference in intensities of the phonon band (first peak). It is evident that the nature of the complex adsorbed on the surface is changing with decreasing pH. The data presented here are insufficient to identify the nature of the modification or, in fact, to distinguish between a diglycine or monoglycine complex.

The tunneling spectra obtained from *trans*-Co(gly)$_2$ are very similar to those obtained from glycine. Its solid-state IR-active metal–nitrogen band at 410 cm^{-1} [22] is not observed, and the rather strong Raman-active Co–N modes (457, 477 cm^{-1}) would be obscured by the glycinate bands. On the basis of the available data, it appears that no cobalt(II) glycine species is present on the surface. That is, the complex merely serves as a source of glycine.

Conclusions

We have demonstrated that IETS is capable of distinguishing between glycine and certain metal complexes of glycine adsorbed on alumina. Although the metal–nitrogen motions can be observed, insufficient information is provided to ascertain the full coordination type of the complexes (i.e., mono, di, cis, trans, etc.). The utility of the method would be greatly enhanced if the usable spectra range was extended to include the metal–oxygen region. In principle, this can be done by utilizing silver or tin in place of lead as top metal.[1,5] Cooling the substrate during the top metal deposition would probably allow one to utilize those metals without degrading the data obtained. Attempts to observe these critical bands are in progress.

The chemical complexity of these systems precludes the use of relative intensities to establish surface configuration. Further, the symmetries of the surface species are so low that the relaxation of optical selection rules which occurs in IETS provides no new information. Unlike the case of the ferrocyanide ion[4,5] where previously unobservable bands appeared as intense features in the tunneling spectrum, no identifiably new bands appear for the glycine complexes studied here. One should recall, however, that IETS has at least one very important advantage relative to infrared studies of adsorption on γ-alumina: it gives access to the 1200–300-cm^{-1} region of the spectrum.

We have demonstrated that certain metal glycine complexes are adsorbed on alumina in preference to dissociative adsorption. An undetermined nickel glycine complex was found to be the most stable species on the alumina surface over a wide range of pH. This range extends beyond the region of stability in water solution. A cobalt(III) glycinate was also

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shown to be a stable surface species. In this case, however, there are indications that the nature of the complex changes with decreasing pH. Further, no evidence was found to indicate the existence of a cobalt(II) glycinate on the surface.

We have also measured the spectrum of the ligand, glycine, adsorbed on alumina at various pH values. While our data are in complete agreement with those of Coleman,[16] we have advanced a modified interpretation of the spectra obtained. We envisage a two-site adsorption process, invoking both zwitterionic glycine and glycinate species, the glycinate being more stable at high pH but present to a large extent throughout the pH 4–9 range.

Subsequent to submission of this article, Brown et al.[36] reported the IETS of several organic amines. They observe the NH stretching motion of NH_3^+ in the 2800-cm^{-1} region. This observation supports the analysis presented in this paper.

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Registry No. gly, 56-40-6; $KCo(gly)_2(NO_2)_2$, 15157-77-4; $Ni(gly)_2$, 13479-55-5; $Ni(gly)Cl$, 76430-69-8; *trans*-$Co(gly)_2$, 14281-74-4; Al_2O_3, 1344-28-1.

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Magnetic Circular Dichroism of Metal-to-Ligand Charge-Transfer Spectra of Hexacarbonyl and Hexacyano Complexes of *n*d^6 Electron Configuration

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Electronic absorption and magnetic circular dichroism (MCD) spectra are reported for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in acetonitrile solution and for $K_4[Fe(CN)_6]$, $K_4[Ru(CN)_6]$, and $K_4[Os(CN)_6]$ in aqueous solution. The spectral pattern observed in the MCD for the two allowed metal-to-ligand charge-transfer (MLCT) bands of $M(CO)_6$ is similar and consists of a positive B term for the band near 3.5 μm^{-1} and a negative B term for the band near 4.4 μm^{-1}. A weak negative A term was also observed at 2.9 μm^{-1} for $W(CO)_6$. The lowest energy allowed MLCT for each $M(CN)_6^{4-}$ complex exhibits a positive A term. The difference between the MCD for the lowest energy MLCT between the $M(CO)_6$ and $M(CN)_6^{4-}$ complexes is discussed in terms of relative metal p-orbital participation in the empty t_{1u} ligand-based MO.

Introduction

The intense electronic absorptions observed in the UV spectra of octahedral metal hexacarbonyl and hexacyano complexes of low-spin d^6 electron configuration were first assigned as metal-to-ligand charge transfer (MLCT) by Gray and Beach in 1963.[1] For example, the two bands near 3.5 and 4.4 μm^{-1} in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were interpreted as electron excitation from the filled, predominantly metal *n*d t_{2g} MO's to empty ligand-based t_{1u} and t_{2u} MO's, respectively (see Figure 1). Both bands were assigned as fully dipole-allowed $^1A_{1g} \rightarrow {}^1T_{1u}$ transitions even though the higher energy band was much more intense. A rationale for the intensity difference took note of the orbital composition of the t_{1u} MO's which contain contributions from the metal $(n + 1)$p orbitals, while the t_{2u} MO's are entirely ligand based. It was suggested that the p-orbital contribution in the t_{1u} MO's was responsible for the smaller transition dipole.[1,2] Similar bands given analogous assignments were identified in the spectra of $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$, though the two allowed transitions were at higher energy and of more equal intensity.[1]

Although the d^6 hexacarbonyl and hexacyano complexes have been the subject of several experimental and theoretical investigations since 1963,[2-8] the MLCT assignments have stood the test and now seem well established. Thus these complexes provide excellent prototypes for the study of MLCT in octahedral symmetry. Therefore as a consequence of our interest in magnetic circular dichroism (MCD) of MLCT transitions in complexes of lower coordination number, we turned naturally to the d^6 hexacarbonyl and hexacyano complexes to extend our understanding of the MLCT process. However there have been surprisingly few MCD studies of octahedral carbonyl and cyano complexes. The paramagnetic d^5 $V(CO)_6$ and $Fe(CN)_6^{3-}$ complexes have been investigated,[9,10] but their spectra are dominated by ligand-to-metal charge transfer (LMCT) and MCD C terms. The MLCT spectra of diamagnetic d^6 carbonyl or cyano complexes should exhibit only A and B MCD terms since the ground state is $^1A_{1g}$ in each case. The only earlier report of MCD for such a complex is limited to MCD spectra of $Fe(CN)_6^{4-}$,[11] in which a positive A term was found for the lowest energy intense band. The sign and approximate magnitude of the A term were shown to be consistent with a MLCT assignment.[11] In view of the limited data available for MLCT transitions of carbonyl and cyano complexes we report here some MCD spectra for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ in acetonitrile and $Fe(CN)_6^{4-}$, $Ru(CN)_6^{4-}$, and $Os(CN)_6^{4-}$ in water.

Experimental Section

The hexacarbonyl complexes were purchased from Alfa-Ventron or Strem Chemicals, Inc., and purified by vacuum sublimation. Vapor-phase and actonitrile solution spectral band energies agreed favorably with previous reports,[1,2] but solution molar absorptivities differed in some cases. The origin of these differences is not known. The complexes are known to be photochemically reactive,[3,4,12] so care

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