indebted to the National Science Foundation for purchase of the Syntex P2$_1$ diffractometer (Grant GP-37028).

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes (Supplementary Tables Ia–Ie), anisotropic thermal parameters (Supplementary Table II), coordinates of the acetone molecule in the crystal structure of **7** (Supplementary Table III), and the crystallographic coordinates of the rigid group atoms (Supplementary Table IV) (111 pages). Ordering information is given on any current masthead page.

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Studies of Solution Character by Molecular Spectroscopy. 8. Ion Sites in Solutions of NaCo(CO)$_4$ in Several Solvents Doped with Cryptand C221

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Abstract: NaCo(CO)$_4$ was dissolved in THF, 1,2-DME, THP, and MTHF and the Na$^+$ complexed with the cryptand C221. In each case, the normal mix of ion sites in the solution was converted into a single ion site. This site was the previously reported solvent-separated ion site of T_d symmetry in the THF and 1,2-DME cases. The new ion site formed in the THP and MTHF solutions shows C_{2v} symmetry. Thus, the anion in THP and MTHF is not isolated from the perturbing influence of the Na$^+$ by complexing the latter with the cryptand, in contrast to the situation in THF and 1,2-DME. Solution structures are proposed for these two kinds of ion sites in the cryptand-complexed salt solutions. Comparison of the infrared spectra of the salt in THF and 1,2-DME solutions doped with C221 with the complex, overlapped spectra of the salt in these neat solvents provides an independent confirmation of the previous report of a computer-aided analysis of the latter spectra and supports its interpretation in terms of ion structures. Altering the normal ion site mix of a solution by adding cryptands provides a very useful tool for the interpretation of its complex vibrational spectrum.

The knowledge of structure at ion sites in solution is fundamental to understanding the physical and chemical properties of ionic solutions. The CO stretching vibrations of the Co(CO)$_4^-$ ion are sensitive to its environment and hence can serve as a probe of solution structure.[1,2] A study has been made of these vibrations in the infrared spectra of several alkali metal salts of the Co(CO)$_4^-$ anion dissolved in several common aprotic solvents.[1-3] The results were interpreted in terms of two kinds of ion-site structures, which were shown to be solvent-separated and contact ion pairs. In the contact site, the cation was found to be associated with the anion in the structure Na$^+$- - -O$\equiv$CCo. Further, the mix of ion sites was seen to vary with solvent, being solvent-separated ion pairs in strong bases (H$_2$O, DMF, Me$_2$SO) and showing an increasing percent of contact pairs as the solvent base strength falls (1,2-DME, THF). Adding a strong donor solvent (DMF, H$_2$O) to salts of this anion in a weaker donor solvent (THF) shifts the ion-site mix to form solvent-separated pairs at the expense of contact pairs.

Similar infrared studies by Brown,[4a] Darensbourg,[4b,5] Pannell,[6a] Rosenblum,[6b] and their co-workers have shown that solvent-separated and contact ion pairs also exist in some nonaqueous solutions containing the metal carbonylate anions Mn(CO)$_5^-$,[4] Mn(CO)$_4$L$^-$,[4b] HFe(CO)$_4^-$,[5] (C$_5$H$_5$)-Fe(CO)$_2^-$,[6] and (C$_5$H$_5$)Mo(CO)$_2^-$.[6a] Contact ion pairs in each of these solutions were found with the Na$^+$- - -O$\equiv$CM structure and a dependence of ion site mix on solvent basicity was also seen insofar as it was investigated.

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Recently, the influence of solution structure on the reactivity of metal carbonylate salts has attracted attention. Collman and his colleagues have studied the kinetics of the alkyl moiety migration in $NaRFe(CO)_4$[7a,b] and of the reaction of $Na_2Fe(CO)_4$ with alkyl halides;[7c] the solvent dependence has been investigated in the reaction of $TlCo(CO)_4$ with PPh_3,[8a] of $NaCo(CO)_4$ and $TlCo(CO)_4$ with $In[Co(CO)_4]_3$,[8a] and of $NaCo(CO)_4$ with R_3SnX.[8b] Darensbourg et al. have examined the kinetics of the reaction of $NaMn(CO)_5$ with RX;[4b] Nitay and Rosenblum have compared the time required to reach a given conversion in the reaction of the Li^+ or Na^+ salt of $[(C_5H_5)Fe(CO)_2]^-$ with epoxides in THF solution.[6b] In all these reactions, ion pairing was found to play a prominent role and significant differences were found in the reactivity of solvent-separated and contact ion pairs.

It can be expected that other kinds of ion site structures exist in metal carbonylate solutions and that they have a role in fixing the chemical and physical properties of these solutions.[9] The extension of the spectroscopic technique to a comprehensive study of structure in such solutions has proved difficult owing to the overlapping of bands from different ion sites in the same solution, overlapping that is sometimes severe and frequently subtle. Instrumental, chemical, and curve analysis methods have been developed to deal with these problems.[10,11] These methods were used in mid-development to show not only the presence of a single ion site in solutions of $NaCo(CO)_4$ in dimethyl sulfoxide, pyridine, dimethylformamide, acetonitrile, hexamethylphosphoramide, and nitromethane but, more significant, that it was populated by the ^{13}C isotopic species $Co(CO)_3C^*O^-$ as well as by the dominantly abundant $Co(CO)_4^-$.[10] With further improvement, they were used to show the presence of one, two, and three sites, respectively, in oxetane, 1,2-dimethoxyethane, and tetrahydrofuran solutions of the salt and to indicate their structures.[11]

The technique used in these recent infrared studies has involved four basic steps: (1) the determination of the *high-resolution* contour of the complex absorption spectrum arising from CO stretching modes of the metal carbonylate ion in the several ion sites of the solution; (2) the computer-aided analysis of the complex contour for the individual bands of which it is composed; (3) the association of each individual band with a vibrational mode of the carbonylate ion in a specific ion site of the solution; (4) the use of the bands found above to characterize each ion site and to obtain information about the solution structure at each site.

A key feature guiding the computer-aided analysis of the overlapped spectral contour is the variation of ion-site populations in a solution by changing its temperature. It provides a means by which the individual bands are sorted out and associated with each ion site. Typically, the temperature covered has ranged from 300 to 150 K. One feels confident in the essential correctness of the analysis for simpler spectral contours.[10,11] Yet it would be desirable to establish the validity of these analyses by independent means. This is especially so since our method detects component bands that are not apparent in a visual examination of the spectra. And one could use help in the interpretation of the more complex spectral curves that have been observed.

The macrobicyclic ligand, cryptand C221, forms a stable inclusion complex with the Na^+ ion in water and in methanol.[12,13] Its role in altering the ion-site populations for salts in polar, aprotic solvents is examined for four $NaCo(CO)_4$ solutions: with 1,2-DME, THF, THP, and MTHF as solvents. At the same time, we examine some aspects of the interaction of the C221 complexed Na^+ with its neighbors.

Experimental Section

Chemicals. The 1,2-dimethoxyethane (DME) used in this study was obtained from Pfaltz and Bauer, Inc., the tetrahydrofuran (THF) from the Fisher Scientific Co., and the tetrahydropyran (THP) and 2-methyltetrahydrofuran (MTHF) from the Aldrich Chemical Co. The $Co_2(CO)_8$ and CaH_2 were from Alpha Inorganics and the molecular sieves (4A, pellets) from Union Carbide-Linde Division. The NaOH was a Mallinckrodt analytical reagent. The macrobicyclic ligand, 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane (cryptand C221), was an EM Chemicals, Inc., product.

$NaCo(CO)_4$ Preparation. The salt $NaCo(CO)_4$ was prepared by the reaction of NaOH with $Co_2(CO)_8$ in THF,[14] using the published procedure.[10] The freedom of the salt from THF and H_2O was established as before.[10]

Solvent and Cryptand Preparation. All solvents were dried in two stages. In the first stage, the solvent was deaerated and vacuum distilled onto CaH_2. After 24 h, it was filtered and subjected to a second 24-h treatment with CaH_2. After filtration, it was stored over molecular sieves, freshly baked under vacuum. The general procedures for handling solvents have been outlined earlier.[10] Solvents prepared in this manner have been tested periodically for residual water. It was found to be less than that which could be detected by the spectroscopic method,[15] i.e., $\leq 3 \times 10^{-5}$ mol H_2O/L solvent. The cryptand was used as received.

Solution Preparation. The $NaCo(CO)_4$ solutions were prepared using the methods of handling described earlier to prevent their contamination with H_2O or reaction with O_2.[10] Stock solutions of $NaCo(CO)_4$ were made by weighing the salt into a volumetric flask and adding solvent to the mark. Stock solutions of C221 in the solvent were prepared in the same way. Solutions of the salt in neat solvent were made for spectroscopic study by mixing aliquot portions of the stock salt solution and the neat solvent; solutions of the salt complexed with the cryptand were prepared for study by mixing aliquot portions of the stock salt solution and the stock cryptand solution. The concentration of these final solutions was selected to provide optimum spectra and was near 1.5×10^{-2} M.

Infrared Spectra. The solutions were run in a standard Barnes-Engineering cell with CaF_2 windows; its path length was 0.053 mm as measured by fringe interference. All the spectra were recorded between 1780 and 2150 cm^{-1} with a Perkin-Elmer Model 180 spectrophotometer using the linear transmittance scale. The slit width varied from 2.1 to 2.4 mm over a run, which corresponds to a resolution change from 0.95 to 1.2 cm^{-1} over this wavenumber range. This is higher resolution than is normally employed for bands as broad as those under study and is expected to be sufficient to reveal all the details of the contour of the absorption complex. The spectra were recorded with an expanded abscissa scale of 1 cm^{-1}/2 mm while the spectrophotometer was operated in the constant I_0 mode at a scan rate of 14 cm^{-1}/min. Under these conditions, there is no significant distortion of the band contour due to tracking error in the pen servo system.[16] Each spectrum was traced twice on the same chart paper. The two tracings superimposed on each other within the noise level of the spectrum.

It is necessary to separate the absorption due to the salt from that arising from the solvent. To this end, the spectra of the solution and of the solvent (or solvent doped with cryptand), in the same cell, were recorded on the same chart. As expected for these dilute solutions, the spectrum of the solution superimposes on that of the solvent on both sides of the absorption complex. This is evidence for the additivity of the absorbance of the salt and solvent in the solution. Consequently, the absorbance of the salt itself (in the solution) was obtained by subtracting the absorbance of the solvent (or solvent doped with cryptand) from that of the solution at each wavelength. In practice, a transmittance file for the solution and for the solvent was formed in the laboratory computer (PDP 11/45) by manually entering the transmittance values read from the chart at each wavenumber throughout the significant wavelength region. The computer then transforms the transmittance into absorbances, makes the subtractions, and forms the absorbance file for salt itself in the solution environment. This file is stored "temporarily" on the "data disk" and also on magnetic tape as a permanent record of the spectrum. This spectrum, or any part of it, may be displayed on the CRT or by the plotter; see Figures 2-7. Moreover, it may be manipulated in any way; e.g., it can be used in an iterative procedure to give the best fit of a model spectrum to the observations or it may be compared to another experimental spectrum, subtracted from it, etc.

Results

$NaCo(CO)_4$ in 1,2-DME. This solution was studied recently

Table I. Infrared Bands from CO Stretching Vibrations of $NaCo(CO)_4$ in Different Ion Sites[10,11]

ion site designation	ion site structure	geometric symmetry	symmetry in vibrations[a]	band frequency,[b] cm^{-1}	symmetry type[a]
I	solvent-separated ion pair/free ion	T_d	T_d	(2004)[c]	A_1
				1887	F_2
I (with isotopic ion[f])	solvent-separated ion pair/free ion	C_{3v}	C_{3v}/T_d	(1992)[d,e]	A_1/A_1
				1887	E/F_2
				1855	A_1/F_2
II	contact ion pair	C_{3v}	C_{3v}/T_d	(2004)[d,g]	A_1/A_1
				1900	E/F_2
				1855	A_1/F_2
III	triple ion	C_{3v}	C_{3v}/T_d	(2007)[d,e]	A_1/A_1
				1906	E/F_2
				1846	A_1/F_2

[a] See footnote 17. [b] Values are characteristic of those found in oxetane, 1,2-DME, and THF. [c] Forbidden in the infrared spectrum; estimated value from Raman spectrum of $NaCo(CO)_4$ in DMF.[14] [d] Forbidden through terms in first order. [e] Estimated value. [f] $Co(CO)_3C^*O^-$. [g] Weak band observed at higher concentrations.

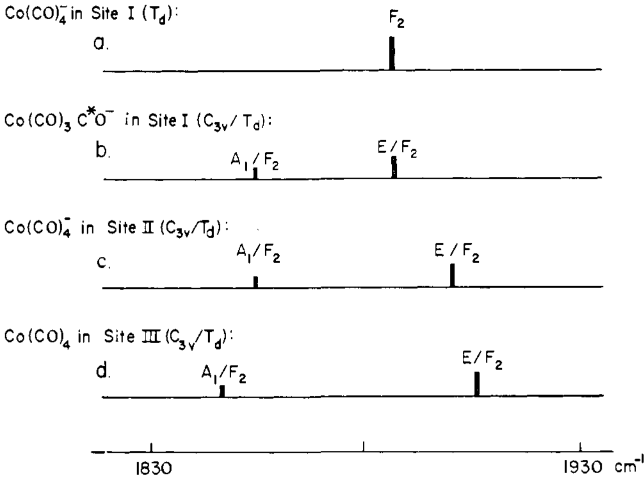

Figure 1. CO stretching frequencies for $Co(CO)_4^-$ in various ion sites.

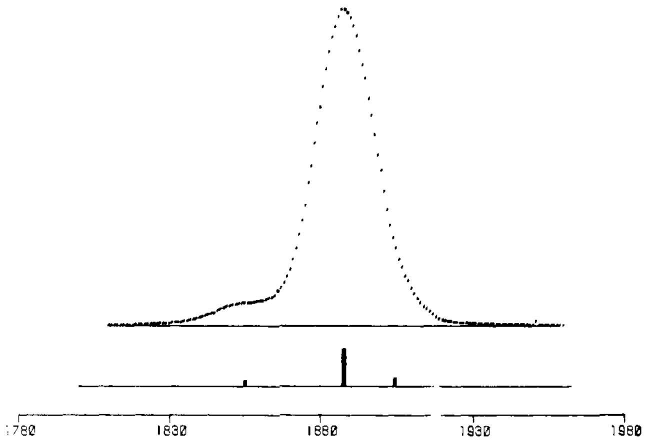

Figure 2. Infrared spectrum of $NaCo(CO)_4$ in 1,2-DME (upper) and its component bands (lower).

by infrared spectroscopy at every 25 K in the temperature range from 200 to 300 K.[11] Two kinds of ion sites were found. Site I, whose population is dominant in this solution, was assigned a solution structure in which the ions have solvent molecules as near neighbors—a result of the bidentate complexing of the Na^+ by 1,2-DME. In addition to this site, about one-seventh of the anions are contact ion paired or, more precisely, they are in a site (site II) whose solution structure may be described as an anion whose near-neighbor shell includes a Na^+ in direct contact with it through an oxygen atom of the $Co(CO)_4^-$ ion.

The effective geometric symmetry at the anion in site I was found to be T_d. As can be seen in Table I, a $Co(CO)_4^-$ ion in such a site calls for the presence of a single infrared band in this spectral region, arising from the triply degenerate F_2 CO stretching modes. Since 1.1% of the C atoms have mass 13 (C*), about 4.4% of the site I locations in the solution are populated with the isotopic ion $Co(CO)_3C^*O^-$. The effective geometric symmetry of this isotopic ion in site I is C_{3v} and its CO stretching modes will follow C_{3v}/T_d dual symmetry selection rules.[17] As can be seen in Table I, the result is that the F_2 band of the normal ion is split into an E/F_2 band and an A_1/F_2 band for this isotopic ion in site I. The positions of these bands are collected in Table I and shown graphically in Figure 1 where the length of the line representing each band is proportional to its intensity obtained by simple approximation.[20]

The anion in the solution structure suggested for site II would be expected to show C_{3v} geometric symmetry because of the intimate interaction of one CO moiety with the adjacent Na^+ ion. The presence of C_{3v}/T_d dual symmetry in these modes leads to a splitting of the F_2 band of site I into two bands in site II, one of A_1/F_2 symmetry and one of E/F_2 symmetry, both of which are expected to be active in the infrared spectrum. The bands assigned to these modes of the anion in site II are shown in Table I and Figure 1c.[11]

Figure 2 shows the spectrum of a 0.015 M solution of $NaCo(CO)_4$ in 1,2-DME at room temperature. Its contour is in agreement with that obtained in the published study.[11] The analysis of this contour yields the three bands whose centers and relative intensities are shown beneath the spectrum of Figure 2.[11] The dominant band at 1887 cm^{-1} was assigned to the F_2 band of the all carbon-12 anion in site I plus the E/F_2 band of the isotopic anion in the same site. The band at 1904 cm^{-1} was attributed to the E/F_2 band of the anion in site II. Its weakness is an indication of the small population of site II in this solution. Both the A_1/F_2 band of the isotopic anion in site I and the A_1/F_2 band of the anion in site II (see Figure 1) were assigned to the weak band at 1854 cm^{-1}.

A DME solution was prepared that contained both the $NaCo(CO)_4$ and the cryptand C221 at an 0.015 M concentration. Its spectrum is shown in Figure 3. To facilitate the comparison of this spectrum with that from the salt in the neat 1,2-DME, the latter spectrum is also reproduced in this figure. A comparison of the two spectra shows that the addition of the cryptand in a 1:1 ratio with the salt removes from the spectrum of the salt in the neat solvent just those bands attributed by the computer-aided analysis to site II and increases the intensity of those bands associated with site I. This result is a direct

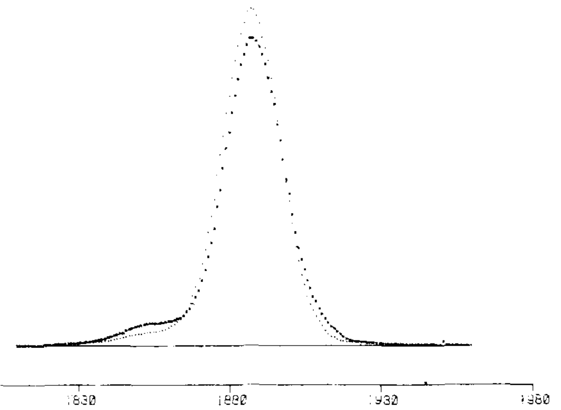

Figure 3. Infrared spectrum of $NaCo(CO)_4 \cdot C221$ in 1,2-DME (·····) and infrared spectrum of $NaCo(CO)_4$ in 1,2-DME (xxxxx).

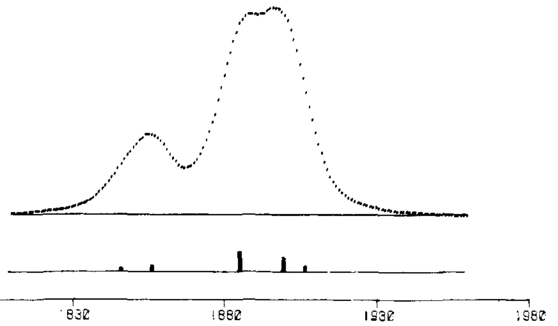

Figure 4. Infrared spectrum of $NaCo(CO)_4$ in THF (upper) and its component bands (lower).

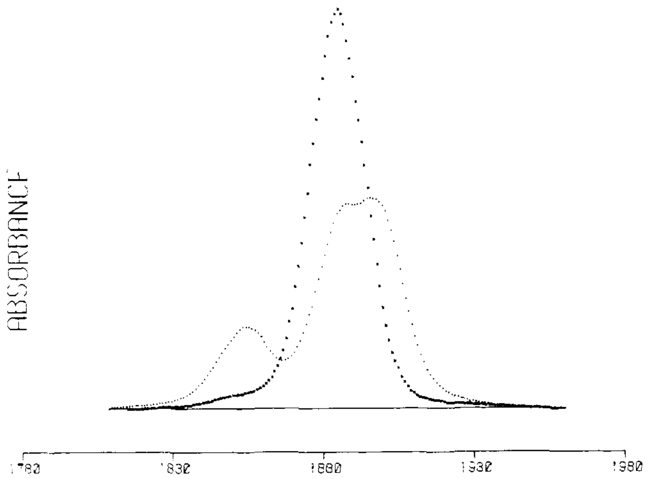

Figure 5. Infrared spectrum of $NaCo(CO)_4 \cdot C221$ in THF (xxxxx), and infrared spectrum of $NaCo(CO)_4$ in THF (·····).

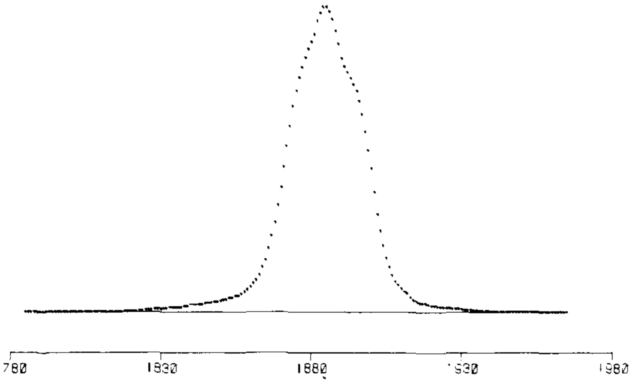

Figure 6. Infrared spectrum of $NaCo(CO)_4 \cdot C221$ in THP.

confirmation of the validity of the published computer-aided analysis.[11] This is all the more significant because the bands associated with site II are not apparent in low-resolution spectra of the neat salt solution nor are they obvious from a visual examination of the high-resolution spectrum of this solution shown in Figure 2.

The finding here that the cryptand produces the conversion site II → site I is also consistent with the structures proposed for sites I and II and the expectation that the cryptand would form an inclusion complex with the Na^+ ion.

$NaCO(CO)_4$ in THF. This solution was studied recently by infrared spectroscopy at every 25 K in the range 150–300 K.[11] Computer-aided analysis of the spectra indicated the presence of three kinds of ion sites: the sites I and II discussed above, present in substantial amounts, and a smaller amount of a site III whose solution structure also places a Na^+ ion in the near-neighbor shell of the anion with direct cation-anion contact at an oxygen atom of the $Co(CO)_4^-$ ion. Electrical conductivity measurements[1] show the presence of some triple ions in this solution and it was suggested[11] that site III may be this kind of structural entity. It was shown that the F_2 band of site I would be expected to split into two infrared-active bands for site III which could be described as an A_1/F_2 and an E/F_2 band in terms of the *local symmetry* (C_{3v}/T_d) at the anion. The bands assigned to these modes of vibration are shown in Figure 1d and Table I.

Figure 4 shows the spectrum of $NaCo(CO)_4$ in THF at room temperature. Its contour is in agreement with that found earlier.[11] Analysis of the spectrum shows it to be composed of the five bands whose centers and relative intensities are given below the spectrum in Figure 4.[11] The band at 1885 cm^{-1} was attributed to the F_2 band of the regular anion in site I and the coincidental E/F_2 band of the isotopic anion in this site. The E/F_2 band from site II is at 1899 cm^{-1} while the A_1/F_2 from this site appears at 1856 cm^{-1} where it coincides with the A_1/F_2 band from the isotopic ion in site I. The 1906-cm^{-1} band was assigned to the E/F_2 band of the anion in site III while the A_1/F_2 band from this site is at 1846 cm^{-1}.

Figure 5 shows the infrared spectrum of a 0.015 M THF solution of $NaCo(CO)_4$ which was also made 0.015 M in C221. To facilitate its comparison with that of this salt in neat THF, its spectrum is also repeated in this figure. One can see that the addition of the cryptand in 1:1 proportion to the salt removes from its spectrum in the neat THF just those bands assigned by the contour analysis to sites II and III and enhances the intensity of the bands associated with site I. This result is completely consistent with the contour analysis shown in Figure 4. The result that the conversion site II, site III → site I takes place when C221 is added to the THF solution of the salt is consistent with the solution structure at the anion attributed to each site and the expectation of the formation of an inclusion complex between the Na^+ ion and the cryptand.

Cryptand Complexed $NaCo(CO)_4$ in THP and MTHF. Figure 6 is the spectrum of a THP solution that is 0.0147 M in $NaCo(CO)_4$ and 0.0150 M in C221. This spectrum is not that of site I! Because the Na^+ is expected to be held in an inclusion complex here also, all three bands are assigned to vibrations of the $Co(CO)_4^-$ ion in a single ion site. This is called site V and its band frequencies, found by the contour analysis of its spectrum, are given in Table II.[21]

The spectrum of the salt in neat THP is complex, overlapped, and relatively insensitive to change in the temperature of the solution. It is not clear how the complex spectrum comes apart into its individual bands nor what bands should be associated together as arising from a single site. But it is clear

Table II. CO Stretching Bands (cm^{-1}) of the $Co(CO)_4{}^-$ Ion in Site V

solvent THP	solvent MTHF
1877.2 (s)	1877.5 (s)
1885.9 (s)	1886.7 (s)
1895.6 (s)	1896.8 (s)
2004 (vw)	2004 (vw)

that several ion sites are present. A comparison of its spectrum with Figure 6 makes it possible to conclude that site V is also present in the salt solution with neat THP and provides an important aid in the interpretation of its spectrum.

A MTHF solution was prepared that contained $NaCo(CO)_4$ and C221 in a 1:1 ratio. The spectrum of the $Co(CO)_4{}^-$ ion in this solution is almost identical with that of Figure 6. Thus, a single ion site is also present in this solution, and it is site V. Computer analysis of this spectrum gives the band frequencies listed in Table II. Note that they are little influenced by the change of solvent from THP to MTHF. One concludes, as expected, that the Na^+ is complexed by the C221 in this solution.

The spectrum of the salt in neat MTHF is complex and overlapped. A comparison of it with the above spectrum shows that site V is present in the uncomplexed salt solution, and provides a key to its interpretation.

Structure at Sites I and V in the Cryptate Solutions. Two kinds of anion sites have been found for $NaCo(CO)_4$ complexed with C221 in the solutions studied here. The structure at these sites is of especial interest because the Na^+ ion is expected to be held within the cavity of the C221 cryptand in both cases. And there is so little difference between the solvents used. For example, there is one more CH_2 group in the cyclic ether THP than in cyclic ether THF, yet site V is formed in the first and site I in the second. Two questions are of importance for each case. What is the nature of the near-neighbor environment of the anion? How is it related to the complexed Na^+ ion?

The change in the spectrum of the anion with ion site shows that the bonding in the $Co(CO)_4{}^-$ ion is sensitive to the nature of its immediate surroundings. Therefore, some insight into this environment may be obtained by computing the force constants for the stretching of the CO bonds of the anion in each site.

As shown in the Appendix, the CO stretching frequencies depend upon composite force constants that are linear combinations of the Co–C and C–O bond force constants, eq 8 and 9. This is the natural consequence of the fact that both Co–C and C–O bonds are deformed in CO stretching vibrations. The composite constant for the CO stretch in a CoCO unit is sensitive to changes in the character of its C–O bond and may be used to follow them.

Since the CO stretching vibrations of the $Co(CO)_4{}^-$ ion in site I show T_d symmetry, all four C–O bonds are equivalent. Thus, the CO frequencies are governed by the constants K and K_i defined in eq 8 and 9. The first is the composite constant for the CO stretch in a CoCO unit and the second is the composite constant for the interaction between two such CoCO units. The values of the force constants obtained by inserting the observed frequencies, 2004 and 1889 cm^{-1}, in eq 3 and 4 are listed in Table III.

The fact that four CO stretching frequencies are observed for the anion in site V (Table II) is not sufficient in itself to fix the symmetry at the anion. If, in fact, two CO bonds were equivalent and differed from the other two, which also were equivalent to each other, the geometric symmetry at the anion would be C_{2v}. Then, the four frequencies would be governed by the constants for the two kinds of CoCO moieties, K' and K'', and the interaction consant K_i (see Appendix). If, however, only one pair of CO bonds were equivalent, the symmetry would be C_s and the four frequencies would be fixed by the four constants: K', K'', K''', and K_i. Lastly, if none of the CO bonds were equivalent, there would be no symmetry at the anion (C_i) and the frequencies would be determined by five constants.

Table III. Composite Force Constants (mdyn/Å) for the CO Stretch in the $Co(CO)_4{}^-$ Ion in Sites I and V

Anion in Site I (T_d)	
K	14.89
K_i	0.45
Anion in Site V(C_{2v})	
K'	14.71
K''	15.00
K_i	0.46

Table IV. Comparison of the Calculated and Observed Frequencies (cm^{-1}) for $Co(CO)_4{}^-$ in Site V. Vibrational Assignment[a]

calcd	obsd	assignment[b]
1877	1877[c]	B_1/F_2
1896	1896[c]	B_2/F_2
2004	2004[c]	A_1/A_1
1886	1886	A_1/F_2

[a] Using the force constants listed in Table III. [b] Made in terms of C_{2v}/T_d dual symmetry (see text). [c] These frequencies used to fix the three force constants.

Since there are more observed frequencies than unknown force constants for the C_{2v} case, an internal test of its validity can be made by noting how well the four frequencies are fit by three force constants. However, if it fails, such a test cannot be made to distinguish between the C_s and C_i models.

Such a test of the C_{2v} model has been made, using the equations (3, 4, and 5) derived in the Appendix. The results are shown in Table IV. They are in excellent agreement with the expectations of this model. The resulting force constants are given in Table III. The (displacements of the) vibrations of the anion are also expected to show the permutation symmetry $S_4 = T_d$ to a good approximation. The assignment of the observed frequencies from site V to the C_{2v}/T_d dual symmetry modes is made in Table IV.

Lehn and co-workers,[23] reasoning from a comparison of the NMR spectrum of the cryptand in solution ($CDCl_3$, D_2O) with that of a variety of salts complexed by the cryptand in the same solvent, concluded that the cation was located in the center of the cryptand in each complexed salt. This view has been supported by X-ray studies of the crystal structure of a variety of salts complexed with cryptands, including the Na^+ complexed with C221.[24] Lehn and Sauvage have measured the equilibrium constant for the formation of the inclusion complex between the Na^+ and C221 in water and in methanol, finding values of 2.5×10^5 and $>10^8$, respectively.[13] The factors that lead to the stability of such complexes have also been examined.[12] They suggest that the inclusion complex should also be stable in the solvents of this research. Consequently, the Na^+ is assigned to the cavity of the cryptand in the solutions under study here.

The presence of the Na^+ ion in the cavity of C221 would be consistent with finding the anion in site I in 1,2-DME and THF. The solution structure at site I has solvent molecules as near neighbors of the anion. Its T_d symmetry has been explained in terms of the equivalence in time of the local conformations that occur at each of the four CO moieties.[11] The finding of C_{2v} symmetry for the anion in site V, however, means that the local environment at two of its CO groups differs from that at the other two.

Figure 7. Structure of $Na^+ \cdot C221$—schematic (A), and solvent structure at window of $Na^+ \cdot C221$ for site I—schematic (B).

A comparison of the CO stretch force constants for the two sites is instructive (see Table III). K', the constant for two of the CO groups of the anion in site V, is smaller than K, its value in site I. The opposite is true for K'', the constant for the other two CO groups of site V. This change in CO bond strength from site I to site V is characteristic of a shift of electron density from the antibonding π orbitals of two CO groups of the anion into the same kind of orbitals for the other two CO groups. It is reasonable to associate this change with the presence of a positive charge in the vicinity of two of the CO groups of the anion in site V.

Figure 7A is a schematic representation of C221. Thus, the cryptand forms a "shell" around the Na^+ in the complex which has three "windows" in it between the $-CH_2CH_2O-$ chains. The chain with one oxygen atom in it is shorter than the other two and this tends to make the window opposite it larger. The Na^+ in the cavity will generate a field outside the shell that varies with position around its circumference and is larger opposite the windows. It should be able to attract and orient polar solvent molecules and anions in the area of these windows, especially the largest one.

These considerations suggest that the anion in site V is held near the window by the field of the Na^+ in the cryptate in a rather well-defined structure of C_{2v} symmetry. The cation and anion are expected to be "close" to each other but are not in contact in the sense that they are in site II.

In the site I cases, a rather well-defined structure is also assumed to exist near the window of the cryptate, as illustrated schematically in Figure 7B. But here it involves solvent molecules only. The anion is relegated to greater, and supposedly variable, distances from the cation in site I, where the behavior of the neighbor solvent molecules leave its inherent T_d symmetry undisturbed. This model is consistent with the observation that it is the better Lewis bases, 1,2-DME and THF, that form site I in the cryptand-doped solutions.

Discussion

The finding that C221 converts the normal ion-site mix of the solution into just one site in each of the four solutions studied is very useful. The ability to see the spectrum of one of the ion sites of a solution free from any contribution from the other sites is an important aid in the interpretation of the solution spectrum and hence in the elucidation of its ion-site structure. This is all the more so in cases like that of the THP solution where the spectrum is complex and the variation of the temperature of the solution has little effect on its spectral contour. Even for solutions with simpler spectral contours, it can be a significant help because of the existence of the subtle overlapping of bands that can occur.

Ligands such as H_2O, DMF, HMPA, NMP, crown ethers, etc., have also been used to drive the ion-site mix of metal carbonylate solutions toward a single site.[1,2,5,6a,7] However, a large excess of the first four ligands is required to reach the single ion site state and this dilutes the substrate solvent and can change its properties. In contrast, no dilution of solvent occurs in the use of the cryptand.

The examination of the high-resolution spectrum of $NaCo(CO)_4$ in DME doped with C221 (Figure 2) confirms the presence of an ion site (II) found earlier with the techniques outlined in the introduction but which is not apparent in low-resolution spectra.[11] The use of these techniques finds a third ion site in the THF solution of $NaCo(CO)_4$[11]—a site not seen in a previous, less advanced study.[3] These results stress how powerful such techniques as high-resolution spectra, computer-aided band contour analysis, and variation of ion site mix are in solution structure studies. Unfortunately, their neglect can lead to error.[25]

The structure models proposed above form the basis for an understanding of what happens in each of these solutions when the cryptand is added to it. Take the THF solution of $NaCo(CO)_4$ as an example. When the cryptand has destroyed the contact ion pair, site II, by removing its Na^+ to the cryptand cavity, it has also destroyed sites I and III, because they are in equilibrium with site II. Thus, the ion site structure I of the neat solution, i.e., $Na^+(THF)_m$, $Co(CO)_4^-$ plus the sites II and III, are replaced by the structure $(Na^+crypt)(THF)_n$, $Co(CO)_4^-$. The latter is also a type I site, with a T_d site I spectrum, because the anion is also solvent surrounded.

The Na^+ ion is placed in the C221 cavity in the model for ion site structure in the solutions of this study because it has been found in this position in a large number of solutions. Thus, the cation is found inside the cryptand cavity for a wide variety of cryptand complexed salts dissolved in $CDCl_3$ and D_2O.[26] Further, the solubility of a number of cryptand complexed salts in organic solvents in which the salt itself has little or no solubility has been interpreted in terms of such a solution structure.[26] Further, an X-ray study of crystalline $[Na^+(crypt)]_2Fe(CO)_4^{2-}$, with crypt = C222, shows each Na^+ ion inside the cavity of its cryptand molecule.[27] And, directly to the point, Popov and coworkers have observed that the chemical shift in ^{23}Na NMR spectra is not influenced either by the solvent or the anion for sodium salts dissolved in some organic solvents and complexed with C221.[28]

To find the $Co(CO)_4^-$ anion in a symmetrical type I site when the Na^+ is complexed by the cryptand (THF and 1,2-DME solutions) was expected. It is generally felt that the cryptate molecule exerts an "isolating" action on the encapsulated cation. For example, the $Fe(CO)_4^{2-}$ anion in crystalline $[Na^+(crypt)]_2Fe(CO)_4^{2-}$ is an essentially undistorted tetrahedron[27] while this anion is distorted in crystalline $Na_2Fe(CO)_4 \cdot 1.5(dioxane)$[29] and $K_2Fe(CO)_4$.[27] This is explained as being due to the fact that the cryptate molecule prevents the Na^+ ion from approaching the $Fe(CO)_4^{2-}$ ion closely enough to cause geometric distortion.[27] One expects the same factors to be at work in the solutions.

The finding of ion site V in the THP and MTHF solutions of cryptand complexed $NaCo(CO)_4$ was not anticipated. The spectrum of the anion here is significant for it is a primary source of information about the nature of this site. The strong F_2 band at 1886 cm^{-1} for the anion in a symmetric site (site I) is split into three components, 1877, 1886, and 1896 cm^{-1}, in site V. There can be no doubt that this is caused by the field of a Na^+ ion associated with the same site. The force-constant calculation indicates that the anion is in an essentially C_{2v} environment, i.e., two CO moieties are much closer to the positive charge than the other two. The simplest model consistent with these facts is the one proposed above, i.e., the anion in the neighborhood of a window of the cryptate molecule with two of its CO moieties pointing in the general direction of the window and the other two away from it. One can readily understand, then, why more basic and more polar solvents (THF, 1,2-DME) would displace the anion from its position opposite the window, forming a site with type I character (T_d symmetry at the anion).

The fact that site V also occurs (as one component of anion mix) in the THP and MTHF solution, even though no cryptand is present, is also significant. When coupled with the obser-

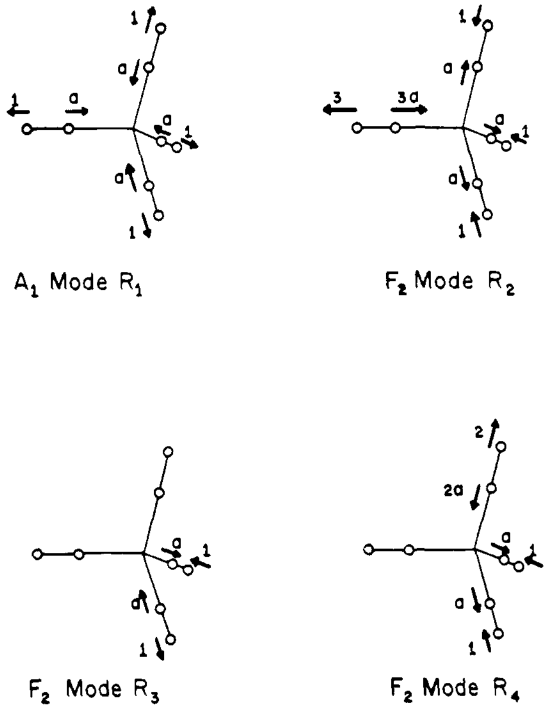

Figure 8. Displacements in the CO stretch modes of $Co(CO)_4^-$ in a T_d site, $a = m_O/m_C$.

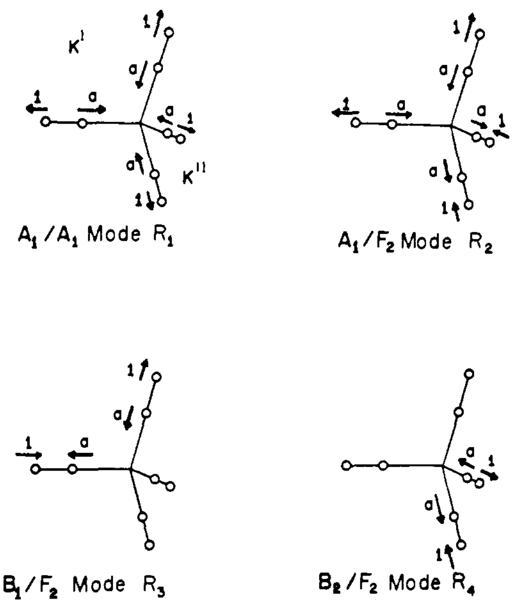

Figure 9. Displacements in the CO stretch modes of $Co(CO)_4^-$ in a C_{2v} site. These displacements normalized by dividing each by $N = 2(m_O + m_C)/m_C$ for equations given in text.

vation that site I appears among the ion sites present in the THF and 1,2-DME solutions of the salt, it would appear that one is dealing here with the second nearest neighbors of the Na^+ ion. Thus, at a type I site, solvent molecules not only occur as the near neighbors of the Na^+ ion but also fill their interstices as second nearest neighbors (and perhaps farther out in the stronger Lewis bases). On the other hand, at site V in the neat THP and MTHF solutions, the $Co(CO)_4^-$ anion is able to replace a solvent molecule in the second nearest-neighbor shell about the Na^+ to give a structure at the anion similar to that formed at the window of the cryptate molecule in the cryptand complexed salt solution. In harmony with this model, site V is formed in the solutions with solvents that are the poorer Lewis bases.

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Appendix

One can calculate the frequency of a single mode of vibration in any molecule without reference to any of the other $3N - 7$ modes of vibratory motion providing that one knows the displacement of every atom in this vibration. The principle behind this statement has been used in a method that calculates the frequencies of the CO stretching vibrations *quite accurately* while, at the same time, being simple and easy to apply because it does not require one to know anything about the other modes of vibration or to take cognizance of them.[21] The method uses the fact that the relative displacements at a CO group

$$\mathrm{M{-}}\underset{a}{\underset{\leftarrow}{\mathrm{C}}}\equiv\underset{1}{\underset{\rightarrow}{\mathrm{O}}} \tag{1}$$

are such that $a = m_O/m_C$, to a good approximation, in these vibrations.[21,30] To obtain the displacements in a given CO stretching mode, one simply uses the displacements of (1) at each CO group in such a way that the requirements of symmetry for the vibration are met. The relative displacements in each of the CO stretching modes of vibration for the $Co(CO)_4^-$ ion for the two cases of interest in this study are shown in Figures 8 and 9. These displacements in a given mode lead directly to its kinetic energy T, the potential energy F, and the frequency ω (in cm^{-1})

$$\lambda = (2\pi c\omega)^2 = F/T \tag{2}$$

through eq 10, 13, and 14 of ref 21.[31]

The $Co(CO)_4^-$ ion in site I shows T_d symmetry. Thus, there is one A_1 mode (R_1) and three, degenerate F_2 modes (R_2, R_3, and R_4) of CO stretching vibration.[18] The displacements in these modes are shown in Figure 8. They readily yield

$Co(CO)_4^-$ in a T_d site

A_1 mode R_1:

$$F_{11} = 4d^2(K + 3K_i)$$
$$T_{11} = 4d^2\mu$$
$$\lambda_{11} = (K + 3K_i)/\mu \tag{3}$$

F_2 mode R_2:

$$\lambda_{22} = F_{22}/T_{22} = (K - K_i)/\mu$$
$$\lambda_{33} = \lambda_{44} = \lambda_{22}$$
$$\mu = m_O m_C/(m_O + m_C),\ d = (m_O + m_C)/m_C \tag{4}$$

where K and K_i are the *composite force constants* defined below in eq 8 and 9.

The C-O stretching vibration of the $Co(CO)_4^-$ ion in a site of C_{2v} geometric symmetry is a good model (see below) for the C-O modes of the anion in site V. Therefore, these modes will show C_{2v} symmetry. They also will show the interchange symmetry $S_4 = T_d$ to the first approximation (four CO moieties). As a consequence, these modes show C_{2v}/T_d dual symmetry and their individual description is A_1/A_1, A_1/F_2, B_1/F_2, and B_2/F_2. The displacements in these dual symmetry modes are given in Figure 9. Their use, as indicated above, leads to the kinetic and potential energy terms and the frequencies given below. Two notes should be made. First, we have simplifed the expressions below by reducing each displacement of Figure 9 by dividing it by $N = 2(m_O + m_C)/m_C$. Second, there is a small, residual coupling between the A_1/A_1 and A_1/F_2 modes that results in the nonzero value for F_{12} and leads to the quadratic secular equation (5).

$Co(CO)_4^-$ in a site with C_{2v} geometric symmetry

A_1/A_1 mode R_1 and A_1/F_2 mode R_2:

$$F_{11} = (K' + K'' + 6K_i)/2$$

$$F_{22} = (K' + K'' - 2K_i)/2$$

$$F_{12} = (K' - K'')/2$$

$$T_{11} = T_{22} = \mu,\ T_{12} = 0$$

The two frequencies are obtained from the two roots λ_{11} and λ_{22} of the quadratic equation

$$\begin{vmatrix} F_{11} - \mu\lambda & F_{21} \\ F_{12} & F_{22} - \mu\lambda \end{vmatrix} = 0 \qquad (5)$$

B_1 mode R_3:

$$\lambda_{33} = F_{33}/T_{33} = (K' - K_i)/\mu \qquad (6)$$

B_2 mode R_4:

$$\lambda_{44} = F_{44}/T_{44} = (K'' - K_i)/\mu \qquad (7)$$

The composite force constant K, associated with the CO stretch in a single CoCO moiety, is defined by

$$K = k + b^2\hat{k} - 2b\bar{k} \qquad (8)$$

where k and $\hat{k}$ are the C-O and Co-C bond stretching constants of the moiety, respectively, and $\bar{k}$ is the interaction constant between the deformation of these bonds in this same CoCO unit.

The interaction between two CoCO moieties is given by the composite force constant K_i defined by

$$K_i = k_i + b^2\hat{k}_i - 2b\bar{k}_i \qquad (9)$$

Here k_i is the interaction constant between the stretching of C-O bonds in two different CoCO units, $\hat{k}_i$ is that between the Co-C bonds in these two units, and $\bar{k}_i$ is the interaction constant between the Co-C bond in one of these CoCO units and the C-O bond in the other unit. The constant b is the ratio of the decrease in the Co-C bond length to the increase in the C-O bond length in the CO vibration. It has the value $b = m_O/(m_O + m_C)$ in the approximation used in this method.

All four CoCO moieties of the $Co(CO)_4^-$ anion in site I are equivalent. Thus, the frequencies are governed by two composite force constants, K and K_i. On the other hand, there would be two different kinds of CoCO moieties in a $Co(CO)_4^-$ ion in an ion site with C_{2v} geometric symmetry, and each would have its own composite constant formed from the bond constants of that moiety by eq 8. These are designated above by K' and K''. There are also three different kinds of composite interaction constants associated with the three different kinds of CoCO moiety interaction in the C_{2v} anion. However, since the three lower frequencies from site V are not split far apart, the anticipated differences in the C-O bonds are small. As a result, one may take the composite interaction constants to have the same value, K_i. The equations given above for the anion in a C_{2v} site were derived on this basis.

Some comments on the method above and on the calculations made with it are in order. When one uses the well-known and practically standard[18] all-modes method of treating the vibrations of a metal carbonyl entity, one finds substantial coupling of the C-O and M-C stretching coordinates in the C-O stretching modes. This coupling accomplishes a selection of atom displacements that will deform both kinds of bonds in the C-O stretching modes. This is the character of the atom displacements to be seen in Figures 8 and 9. In fact, an all-modes calculation on the $Co(CO)_4^-$ anion in site I (T_d) finds the C-Co/C-O displacement ratio to be 1.41 for the A_1 mode and 1.45 for the F_2 modes. This ratio does not change significantly from one metal carbonyl moiety to another. The ratio used in the modes of Figures 8 and 9 is 1.33. One sees that our simple modes contain almost all of the coupling found in the all-modes treatment. While our displacements are not exact, nevertheless, they are eminently satisfactory for calculating the C-O frequencies. This follows from the application of a well-known perturbation result to vibrational calculations, i.e., the use of a set of atom displacements in a mode of vibration that is correct to the zero order of approximation will yield a frequency of vibration that is correct up to but not including terms of second and higher order of approximation. Just what that means in C-O stretching frequency calculations can be seen from the results of an all-mode calculation for the $Co(CO)_4^-$ ion in the T_d site, which shows that an error of 1 cm^{-1} (in 2004 cm^{-1}) is made in the A_1 frequency and 1.3 cm^{-1} (in 1889 cm^{-1}) is made in the F_2 frequency by the approximation! This affects K by only ca. 0.02 mdyn/Å and is negligible for the purposes of this application.

An insight into how composite force constants arise can be obtained from a consideration of the potential energy V generated by the atom displacements at one CO group of the anion in site I in any one of its modes of vibration depicted in Figure 8. One has

$$2V = k\Delta r^2 + \hat{k}\Delta R^2 + 2\bar{k}\Delta r\Delta R$$

for these displacements where $\Delta r = 1 + a$ is the distortion of the C-O bond, $\Delta R = -a$ is that of the C-Co bond, and $\Delta R = (-a/(1 + a))\Delta r = -b\Delta r$ expresses the fixed ratio between these two bond distortions. Making use of this relation between ΔR and Δr, the potential energy becomes

$$2V = (k + b^2\hat{k} - 2b\bar{k})\Delta r^2 = K\Delta r^2$$

This gives eq 8 for K. Thus, the composite force constant K describes the total force that resists this distortion of the anion. Since this distortion takes place in solution, there is a contribution to k, $\hat{k}$, and $\bar{k}$ arising from the presence of the adjacent solvent molecules.[32] The part of k that comes from the solvent molecules is expected to comprise several percent of it. While not negligible, it indicates that the dominant part of k comes from the C-O bond contribution. The same is true of $\hat{k}$ and $\bar{k}$.

For the anion in site V, one must add the consequences of the presence nearby of the Na^+ ion in its cryptate molecule to the above considerations. The electrical potential of the Na^+ falls off slowly with distance from the cation (as $1/r$ in continuum dielectric theory). It affects the potential energy of the $Co(CO)_4^-$ ion in two ways. First, it polarizes the anion, an effect that is described by a change in the character of the anion bonds. Second, it interacts Coulombically with the (polarized) charge distribution of the anion. The first effect appears in the values of the bond contribution to the force constants k, $\hat{k}$, and $\bar{k}$ and, hence, adds no new terms to the treatment above. This change, due to the presence of the Na^+ and primarily to be seen in k, is found to be substantial for the $Na^+Co(CO)_4^-$ ion pair in site II and can be expected also to be significant in site V, although smaller. This dropoff results from the fact that the Na^+ is farther away from the $Co(CO)_4^-$ ion in site V; the estimated Na^+- - -Co distance there is 7.8 Å. The Coulombic contribution from the Na^+ appears as part of the values for k, $\hat{k}$, and $\bar{k}$.[33] One can get an order of magnitude estimate of 3 × 10^{-4} mdyn/Å for this contribution to k.[34] One concludes, therefore, that these Coulombic contributions to k, $\hat{k}$, and $\bar{k}$ may be neglected in assessing the significance of these constants. The contribution of the adjacent solvent molecules plus the cryptate molecule appears in k, $\hat{k}$, and $\bar{k}$. Their contribution is expected to be very nearly the same as in site I.

The values of K, K', and K'' obtained from the frequencies of the observed spectral bands using eq 3-7 are found in Table II. One is now in the position to assess what the differences $K - K'$ and $K - K''$ mean. These constants are related to the values of k, $\hat{k}$, and $\bar{k}$ for each of the different bonds by eq 8. Since $k \sim 15$, $\hat{k} \sim 3$, and $\bar{k} \sim 0.5$, all in units of mdyn/Å, and little difference is expected in the values of $\hat{k}$ and $\bar{k}$ betweeen site I and site V, then one expects $\Delta k \gg \Delta\hat{k} > \Delta\bar{k}$ and hence that $K - K'$ and $K'' - K$ are dominated by Δk. The value of k was seen above to be dominated by the C-O bond strength but to have a nonnegligible contribution from the adjacent solvent molecules (plus the cryptate molecule). It has been observed that the frequency of the F_2 CO stretching band from the $Co(CO)_4^-$ anion in site I is almost completely independent of solvent for a group of $NaCo(CO)_4$ solutions in which the solvents spanned a wide range of chemical character, size, shape, dipole moment, dielectric constant, and electron pair donor ability.[10] This means that changing the solvent has little influence on the value of k. One concludes, therefore, that the values of ΔK observed in this study will primarily reflect the change in the C-O bond strength caused by the polarization of the anion by the nearby Na^+ in site V.

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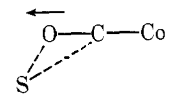
(20) A calculation very much like that illustrated in the Appendix of this paper gives the listed values for the isotopic ion. In particular, in the approximation used for the motion of the atoms at each CO moiety, the E/F_2 CO band frequency of the isotopic ion should coincide with the F_2 CO band of the normal ion (no motion of C* is involved). Tests made for the normal ion (and similar cases[21]) indicate that CO stretching frequencies calculated with this approximation lie within ca. 1 cm^{-1} of the values calculated without approximation. The additional effect on the E/F_2 frequency of changing one carbon atom to its isotope can be expected to be smaller than this 1 cm^{-1} because it can arise only from the coupling of certain *low-frequency* bending modes with C* motion to the E/F_2 CO stretching modes—an occurrence expected to be small. In no experimental case where only site I occurs have we been able to resolve the E/F_2 band of the isotopic ion from the F_2 band of the normal ion. The value given for the E/F_2 band of the isotopic ion in Table I and Figure 1 is the experimental value for this E/F_2-F_2 band. To add further credence to this procedure, the observed frequency of the A_1/F_2 band is in excellent agreement with its value computed by this approximation.[10]
(21) W. Edgell in "Infrared and Raman Spectroscopy", Part A, E. Brame, Jr., and Jeannette Grasselli, Eds., Marcel Dekker, New York, 1976, pp 256-265, and references cited therein.
(22) We have been following the practice of numbering the ion sites in the chronological order of their observation. There is an ion site IV. It will be the subject of a forthcoming publication.
(23) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2889 (1969).
(24) (a) R. Weiss, B. Metz, and D. Moras, Proceedings of the XIII International Conference on Coordination Chemistry, Warsaw, Poland, 1970, Vol. II, p 85; (b) B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 444 (1971); (c) D. Moras and R. Weiss, *Acta Crystallogr., Sect. B*, **29**, 396 (1973); (d) *ibid.*, **29**, 400 (1973); (e) D. Moras, B. Metz, and R. Weiss, *ibid.*, **29**, 383 (1973); (f) *ibid.*, **29**, 388 (1973).
(25) For example, the reactivity of $NaCo(CO)_4$ with $(CH_3)_3SnCl$ and Ph_3SnCl has been studied in five ethers.[8b] The reaction goes in 1,2-DME. Only the bands expected from the solvent-separated ion pair (site I) are apparent in the low-resolution spectrum. Before the high-resolution study was made, it was concluded that the reaction takes place in DME as site I and one could write

$$\frac{d(\text{products})}{dt} = k_s(\text{I})(\text{RX}) \qquad \text{(A)}$$

But evidence will be presented to support the idea that the reaction takes place at the contact ion pair, site II. Then, the value of k_s would really be kK, where K is the equilibrium constant in the reaction forming II from I and k is the rate constant for the reaction as it takes place, i.e., when the right-hand side of eq A is replaced by k(II)(RX). The meaning assigned to the activation energy obtained from k_s would also be wrong.
(26) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron*, **29**, 1647 (1973).
(27) R. G. Teller, R. F. Finke, J. P. Collman, H. B. Chin, and R. Bau, *J. Am. Chem. Soc.*, **99**, 1104 (1977).
(28) A. Popov, private communication.
(29) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **98**, 2434 (1976).
(30) W. Edgell and R. Moynihan, *J. Chem. Phys.*, **27**, 155 (1957).
(31) Occasionally, there are two CO stretching frequencies of the same symmetry. Then it is necessary to solve a quadratic equation to obtain the frequencies.
(32) One can readily show that k contains a contribution from the adjacent solvent molecules with the help of the diagram shown. Here S represents



a solvent molecule; an oxygen atom of the anion has been displaced while all other atoms of the system are kept fixed in position. The force resisting this distortion clearly arises from two sources: the distortion of the C-O bond and the interaction of S with the O atom. But both the force from the distortion of the C-O bond and that from the interaction of S with O are proportional to the change in the C-O bond length Δr, for the displacement of the diagram, and hence may be added together to give the net force $k\Delta$r. Thus, the force constant k has a contribution arising from the presence of solvent molecules as well as from the distortion of the C-O bond when the anion vibrates in solution. In similar ways, one can show that $\hat{k}$ and $\bar{k}$ also contain such contributions.
(33) The argument is exactly the same as that given for the solvent molecule.[32]
(34) The vibration of the Na^+ ion in a "cage" of solvent molecules much like those used in this study has been observed in the far-infrared near 180 cm^{-1}.[35,36] One can obtain a composite (net) force constant from this value, most of which was shown to arise from ion-molecule repulsion.[35c] Taking 0.05 mdyn/Å for an order of magnitude estimate of the Coulombic part and taking into account the much greater distance between the Na^+ ion and an oxygen atom of the anion in site V than one expects between a Na^+ ion and an oxygen atom of a neighbor solvent in a pure salt solution plus the necessity to project the C-O distortion along the Na^+- - -O line (multiplies the remnant by a $\cos^2 \alpha$) yields an order of magnitude estimate for the Coulombic contribution to k from Na^+ of about 3×10^{-4} mdyn/Å.
(35) (a) W. F. Edgell and A. T. Watts, Abracts, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1965, p 85; (b) W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. Risen, Jr., *J. Am. Chem. Soc.*, **88**, 1815 (1966); (c) W. F. Edgell, J. Lyford, IV, R. Wright, W. Risen, Jr., and R. Watts, *ibid.*, **92**, 2240 (1970).
(36) (a) B. D. Maxey and A. I. Popov, *J. Am. Chem. Soc.*, **89**, 2230 (1967); (b) *ibid.*, **91**, 20 (1969); (c) J. L. Wuepper and A. I. Popov, *ibid.*, **91**, 4352 (1969); (d) W. J. McKinney and A. I. Popov, *J. Phys. Chem.*, **74**, 535 (1970).