

Studies of Some Aspects of Solution Character by Molecular Spectroscopy. V. Identification, Population, and Equilibrium of the Anion Sites for $\text{NaCo}(\text{CO})_4$ in Tetrahydrofuran¹

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Abstract: The infrared and photoelectric laser-Raman spectra of $\text{NaCo}(\text{CO})_4$ in the THF solutions were examined in the CO stretching region. Temperature variation of the complex infrared band envelope reveals the presence of two kinds of anion environment and permits the spectra to be divided into four band components. A study was made of the variation of these band components with salt concentration in the range from 0.03 to 0.0007 *M* and with temperature from 29 to -42° . Adding the results of these studies to a comparison of the spectra with selection rules for the most probable anion sites permits the major anion sites in this concentration range to be identified as solvent-separated ion pairs and contact ion pairs. The attachment of the cation to the anion in the contact pair is indicated as monodentate. It is considered most likely that cations in both sites are contributing to the single far-infrared band which has been associated with the Na^+ vibration. The CO stretching frequency assignments are $F_2 = 1886$, $A_1 = 2005$ for the solvent-separated ion pair and $A_1 = 1855$, 2005 , $E = 1898 \text{ cm}^{-1}$ for the contact ion pair. The molar integrated intensity for each vibration in the infrared was approximated by an extrapolation procedure and leads to the population of the anion sites. The equilibrium constant for the conversion of contact pairs to solvent-separated pairs at 29° obtained in this way is $K = 0.45$ with $\Delta H = 3.7$ kcal and $\Delta S = 14 \text{ eu}$. The ΔH value is compared with that for two sodium carbanions in THF and the differences are interpreted in terms of the basic steps involved in the conversion of a contact ion pair into a solvent-separated ion pair.

In the preceding paper,² it was shown that the $\text{Co}(\text{CO})_4^-$ ion exists in two different kinds of environment in THF solutions of $\text{NaCo}(\text{CO})_4$. Each kind of environment can arise from at least two different anion sites (e.g., free ions, contact ion pairs, etc.). One objective of this research was to identify the anion sites associated with each kind of environment. Another was to determine the population of each site and to evaluate the thermodynamics of the equilibria involved. To these ends, we have examined the CO stretching region of the infrared and Raman spectra of $\text{NaCo}(\text{CO})_4$ in THF, divided the complex bands into components, and compared the results with theoretical expectations for the more probable anion sites. In addition, the variation of the components of the complex infrared band with gross salt concentration and with temperature change has been studied. The results have been examined for their implications.

Experimental Section

The experimental details involved in obtaining the infrared spectra are outlined in the preceding paper.² Cell thicknesses were determined by the interference-fringe method. The low-temperature cell is shown in Figure 1. The cell body was made of copper. Silicone O rings were used to effect the seals between the two cell pieces and between them and the cell windows. The cell was filled through the threaded port in the top which was sealed by a screw which was tightened onto an O ring via a washer. It was found useful in maintaining the vacuum tightness of the cell to cover this O ring with stopcock grease where it contacted the metal surfaces. Cell windows were of Irtran-2 ground to a thickness of 0.5 mm and polished. Thermal insulation was provided by the vacuum jacket shown in Figure 2. It is made of a glass $\text{F} 71/60$ joint sealed to a Kovar cup which, in turn, is silver soldered to the copper block in which the cell is mounted. The KBr windows of the jacket were sealed to it with Glyptal. The temperature of the cell was measured with an iron-constantan ther-

mocouple in intimate contact with it. Refrigerant was added to the cup in such quantities and at such frequencies as to maintain the desired temperature level. Through this method, it was possible to keep the temperature constant during the course of a run to $\pm 2^\circ$.

The Raman spectra were excited by a He-Ne laser (Spectra Physics, Model 125) and the 6328-\AA exciting line was isolated from sundry weak emissions by a spike filter. The spectra were recorded photoelectrically by photon counting with both a Spex Industries and a Jarrell-Ash Raman spectrophotometer. Polarization measurements were made by taking the ratio of the intensity with the polarization vector of the laser beam before the sample set parallel to the direction of observation to that with it set perpendicular while the analyzer is set to pass the vector perpendicular to the slit.

The solvents² and the salt³ were prepared as previously described. Concentrations were determined by analyzing for Co by the nitroso-R salt method.⁴

Results

The infrared spectrum of $\text{NaCo}(\text{CO})_4$ in THF shows two bands in the CO stretching region. A weak band of simple form appears at 2003 cm^{-1} , while the very strong band of complex envelope is found at about 1890 cm^{-1} . This band changes its envelope as the temperature is lowered. As can be seen in Figure 3, the intensity of the band falls in the region near 1855 cm^{-1} , increases near 1886 cm^{-1} , and falls again at higher frequencies. This finding is in striking similarity to what happens when water is added to this solution.² In consequence, the band can be divided into three components corresponding to the three areas which change. This was done with the aid of a Du Pont curve resolver using a band-shape intermediate between that of the Gauss and the Lorentz form. Because of the form of the Beer-Lambert law, the decomposition of the band into components was done on the absorbance curve

(1) Based in part on the Ph.D. thesis of J. Lyford, IV, Aug 1969.

(2) W. F. Edgell, J. Lyford, IV, A. Barbetta, and C. I. Jose, *J. Amer. Chem. Soc.*, **93**, 6403 (1971).

(3) W. F. Edgell and J. Lyford, IV, *Inorg. Chem.*, **9**, 1932 (1970).

(4) W. F. Edgell, M. T. Yang, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 2563 (1965).

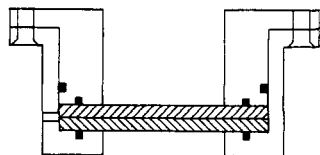


Figure 1. The low-temperature infrared cell. ● indicates O rings; the cross-hatched areas are the windows.

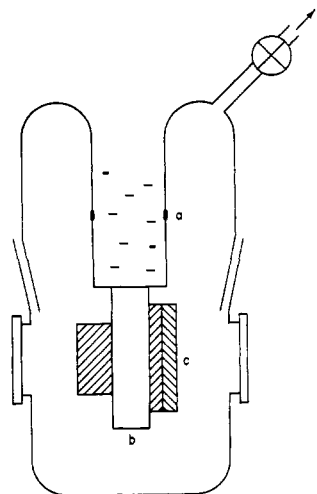


Figure 2. The vacuum jacket for the low-temperature cell showing the cell in place.

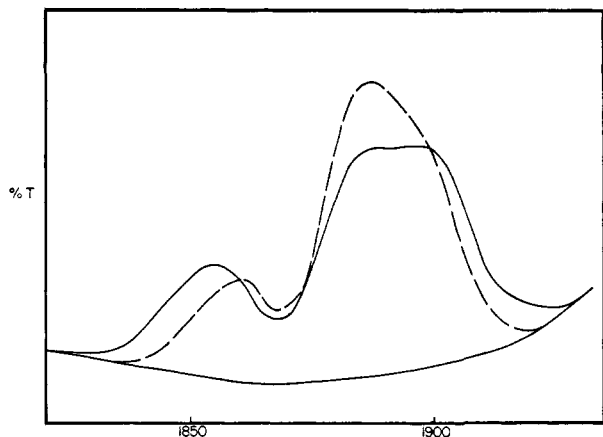


Figure 3. The 1890-cm^{-1} infrared band of $\text{NaCo}(\text{CO})_4$ dissolved in THF: —, at 29° ; ---, at -20° .

rather than the transmission curve. The results are shown in Figure 4 for a 0.025 M $\text{NaCo}(\text{CO})_4$ solution. The frequencies of the several infrared band components are collected in Table I. Those at 1855 , 1898 , and

Table I. Anion Frequencies (cm^{-1}) and Assignments for the Infrared and Raman Band Components from $\text{NaCo}(\text{CO})_4$ in THF

Environment	Infrared	Raman	Assignment
Kind I	1886	$1889 (0.76)^a$	T_d, F_2
		$2005 (\sim 0.1)$	T_d, A_1
Kind II	1855	$1857 (0.74)$	C_{3v}, A_1
		$1905 (0.76)$	C_{3v}, E
		2003	$2005 (\sim 0.1)$

^a Single depolarization measurement made at band maximum at 1890 cm^{-1} .

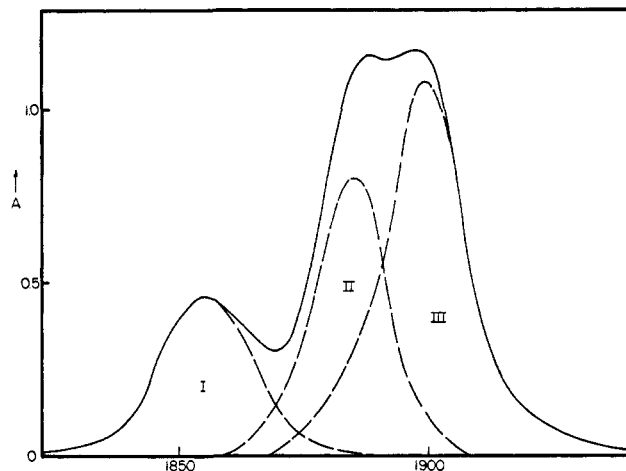


Figure 4. The division of the 1890-cm^{-1} infrared band into components.

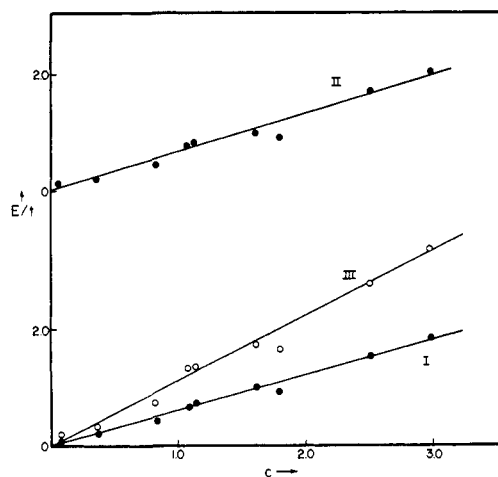


Figure 5. Plot of E/t vs. salt concentration for the three infrared band components. E/t is in units of 10^2 cm^{-2} , c is in 10^{-3} M .

2003 cm^{-1} are assigned to one kind of anion environment because they move together with temperature change, while that at 1886 cm^{-1} is assigned to another kind because it moves in the opposite way to the former components.

It is natural now to inquire how these band components vary with salt concentration. To answer this question, the infrared spectrum in the 1900-cm^{-1} region was obtained for $\text{NaCo}(\text{CO})_4$ solutions in the concentration range from 0.0007 to 0.03 M . The absorbances were computed, the absorbance vs. frequency curves plotted, and the latter resolved into the three components. The curve resolver yields these areas in arbitrary units. To convert them to the proper units, the total area under the absorbance vs. frequency curve for each band was obtained by planimeter and divided into three parts in proportion to the area values obtained by the curve resolver. Each such area is the integrated absorbance (E) for that band component, e.g., $E_I = \int \log(T_0/T)_I d\nu$. The results are collected in Table II and plotted in Figure 5. Two conclusions may be drawn at once. The first is that the integrated absorbance for each component varies linearly with gross salt concentration. The second is that the ratios

Table II. Integrated Absorbances (E) for Infrared Band Components Due to Anion for $\text{NaCo}(\text{CO})_4$ in THF at Various Salt Concentrations

Concentration, M	t , mm	E_I/t^a	E_{II}/t^a	E_{III}/t^a
6.69×10^{-4}	1.033	1.22	1.22	2.05
3.67×10^{-3}	0.522	1.89	1.89	3.17
8.31×10^{-3}	0.205	4.20	4.20	7.45
1.08×10^{-2}	0.0390	6.61	7.86	13.85
1.13×10^{-2}	0.0390	7.50	8.17	13.76
1.61×10^{-2}	0.0390	9.90	9.90	17.40
1.80×10^{-2}	0.0830	9.14	9.14	16.73
2.51×10^{-2}	0.0390	15.27	16.95	27.87
2.97×10^{-2}	0.0390	18.42	20.37	34.35

^a Units for E/t , 10^2 cm^{-2} .

of the integrated absorbance of the band components assigned to the two kinds of anion environments, E_I/E_{II} and E_{III}/E_{II} , are independent of salt concentration in this concentration range.

The integrated absorbance for a band component is related to the concentration (c) of the anion in that kind of solution environment which produces it, the infrared cell thickness (t), and the molar integrated intensity (B) for the band component. Thus, one has the relations

$$\begin{aligned} E_I &= c_I t B_I \\ E_{II} &= c_{II} t B_{II} \\ E_{III} &= c_{III} t B_{III} \end{aligned} \quad (1)$$

Since components I and III are assigned to the same kind of environment, one expects to find that $c_I = c_{III}$. If one has values for the B 's, one can compute the anion population in each kind of environment (the c 's). But both the c 's and the B 's are unknown. The usual treatment of this kind of problem to obtain the B 's is to extrapolate the E vs. salt concentration data to limits where only one kind of environment prevails. However, the fact that E_I/E_{II} and E_{III}/E_{II} are independent of concentration makes this approach impossible. Yet it is not unreasonable to expect that the B 's are temperature independent, and this provides a method to estimate their values. It was found above that decreasing the solution temperature increased the absorption of band component II while decreasing those of I and III. Therefore, extrapolation of E vs. temperature data to 0°K will provide a value of B_{II} . Conversely, extrapolation to infinite temperature will provide values for B_I and B_{III} . These extrapolations are best done by combining eq 1 with

$$c = c_I + c_{II} = c_{III} + c_{II} \quad (2)$$

to obtain the relationships

$$E_I/c = tB_I - (tB_I/tB_{II})(E_{II}/c) \quad (3a)$$

$$E_{III}/c = tB_{III} - (tB_{III}/tB_{II})(E_{II}/c) \quad (3b)$$

Here c is the salt concentration at the temperature to which the experimental values of E_I , E_{II} , and E_{III} apply. According to eq 3a, a plot of the values of E_I/c at the several temperatures against the corresponding values of E_{II}/c should yield a straight line. Extrapolation of this line to the intercept $E_{II}/c = 0$ gives the value of tB_I and extrapolation to the intercept $E_I/c = 0$ gives tB_{II} . Similar extrapolation of the straight line of eq 3b to the intercepts gives tB_{III} and a second, independent evaluation of tB_{II} . Table III gives the experi-

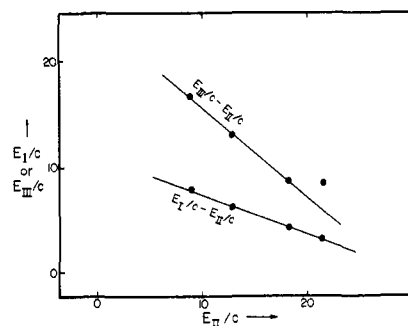


Figure 6. The reciprocal relation of E_I/c to E_{II}/c and E_{III}/c to E_{II}/c . The units are $10^2 \text{ l.}/(\text{mol cm})$. Intercepts (see text) are $tB_I = 11.2$, $tB_{II} = 29.5$, $tB_{III} = 24.2$, $tB_{II} = 28.4$ in the above units.

mental data for the temperature-variation runs. Concentrations at lower temperatures were obtained from the room-temperature value by correcting for the volume change of the solution using the density data of Szwarc and coworkers for THF.⁵ Figure 6 shows the integrated absorbances at the several temperatures plotted in the manner of eq 3. Straight lines are indeed found and the intercepts give $B_I = 8.39$ and $B_{II} = 22.0 \times 10^4 \text{ l.}/(\text{mol cm}^2)$ from eq 3a and $B_{III} = 18.1$ and $B_{II} = 21.2 \times 10^4 \text{ l.}/(\text{mol cm}^2)$ from eq 3b. These values were used to calculate the concentrations of the two kinds of anion environment at the several temperatures, with the results to be found in Table III. With

Table III. Integrated Absorbances (E) for Infrared Band Components Due to Anion for $\text{NaCo}(\text{CO})_4$ in THF at Various Temperatures. Concentrations of Kinds of Anion Environment

Temp, $^\circ\text{C}$	[Salt], c , $10^{-3} M$	E_I/c^c	E_{II}/c^c	E_{III}/c^c	c_I ,	c_{II} ,	c_{III} ,
					$10^{-3} M$	$10^{-3} M$	$10^{-3} M$
29	4.24	7.92	9.00	16.56	3.00 ^a	1.29 ^a	
						1.34 ^b	2.90 ^b
2	4.36	6.22	12.91	12.96	2.41	1.91	
						1.98	2.33
-20.5	4.48	4.10	18.35	8.67	1.64	2.78	
						2.89	1.61
-42	4.58	3.18	21.51	8.43	1.30	3.33	
						3.46	

^a This pair is evaluated from the intercept pair (see text) $B_I = 8.39$, $B_{II} = 22.0$. ^b This pair is evaluated from the intercept pair $B_{III} = 18.1$, $B_{II} = 21.2$. B is in units of $10^4 \text{ l.}/(\text{mol cm}^2)$. Cell thickness 0.134 mm. ^c Units for E/c , $10^2 \text{ l.}/(\text{mol cm})$.

the exception of the one point which is clearly off the straight line, good agreement is obtained between the concentrations calculated from each pair of B values. Note that $c_I = c_{III}$ within the limits of the measurements.

The formation of an anion in an environment of the first kind (band component at 1886 cm^{-1}) from an environment of the second kind (band components at 1855 , 1898 , and 2003 cm^{-1}) is clearly exothermic. The thermodynamic quantities accompanying this process can be approximated from the data of Table III. Averaging the concentrations determined in the two ways yields the equilibrium constants found in Table IV and whose temperature variation is shown in Figure 7.

(5) C. Carvajal, K. Tolle, J. Smid, and M. Szwarc, *J. Amer. Chem. Soc.*, **87**, 5548 (1965).

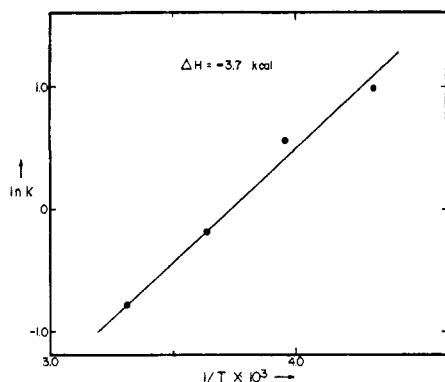


Figure 7. The temperature variation of $\ln K$ for conversion of kind II environment to kind I environment.

From the slope of the straight line representing the $\ln K$ vs. $1/T$ data, one obtains $\Delta H = -3.7$ kcal for the process. Combining the values of $\ln K$ with ΔH yields the entropy changes tabulated for the process. A constant value of $\Delta S = -14$ eu is obtained.

Table IV. Thermodynamic Quantities for the Process $\text{Co}(\text{CO})_4^-$ (kind II) = $\text{Co}(\text{CO})_4$ (kind I)

Temp, °C	K	$\Delta H^\circ/T$, cal/(°K mol)	ΔS° , cal/(°K mol)
29	0.45	-12	-14
2	0.82	-13	-14
-20.5	1.8	-15	-13
-42	2.6	-16	-14

In order to aid in the identification of the kinds of environment in which the anion is found in these solutions, photoelectric tracings of the laser-Raman spectra of $\text{NaCo}(\text{CO})_4$ in THF were made for the C-O stretching region. Figure 8 shows such a run after the background count has been subtracted. The strong band centering at about 1890 cm^{-1} is clearly complex and, indeed, the Raman spectrum is very similar to the infrared spectrum. The strong Raman band is divided into three components whose centers are listed in Table I and which are located on Figure 8 by arrows. Polarization measurements were made at the center of the 2003-cm^{-1} band and at 1855 and 1889 cm^{-1} for the strong band, with the results listed in Table I.

Discussion

The shape of the envelope of the strong infrared band centered about 1898 cm^{-1} together with the variation in this shape as the solution temperature is changed leads to the conclusion that there are two kinds of solution environments for the $\text{Co}(\text{CO})_4^-$ ion in $\text{NaCo}(\text{CO})_4$ solutions in THF. The Raman band also shows a similar complexity. The frequencies of vibration of the anion in these two kinds of environment (see Table I) may be compared with the theoretical expectations for the $\text{Co}(\text{CO})_4^-$ ion in several kinds of solution structure. In assessing the amount and character of the solvent interactions with the anion, it is good to recall that CCl_3H , as well as water, hydrogen bonds to the NO_3^- ion in solution.^{6,7} THF may be expected to interact

(6) D. E. Irish and A. R. Davis, *Can. J. Chem.*, **46**, 943 (1968).

(7) A. R. Davis, J. W. Macklin, and R. A. Plane, *J. Chem. Phys.*, **50**, 1478 (1969).

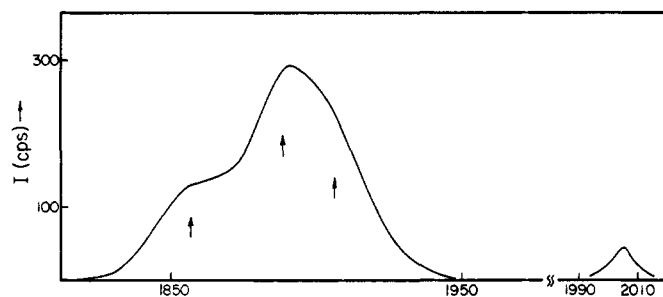


Figure 8. The laser-Raman spectrum of $\text{NaCo}(\text{CO})_4$ dissolved in THF in the CO stretching region. Arrows indicate band components.

weakly with the $\text{Co}(\text{CO})_4^-$ ion, possibly through hydrogen bonding to its oxygen atoms. Because this interaction is expected to be weak, almost all of the force resisting the stretch of the CO groups is expected to come from within the anion. When the $\text{Co}(\text{CO})_4^-$ ion finds only THF molecules in its near-neighbor environment, the CO stretching motion will take place in a tetrahedral field if the interaction with the THF molecules is either negligible or essentially equal at each CO group. Such a situation is expected to apply when the anion moves independently of the cation. Then, T_d symmetry applies and one triply degenerate (F_2) frequency can appear in both the infrared and Raman spectra as well as one nondegenerate (A_1) frequency which is only active in the Raman spectrum. The F_2 frequency will give a strong band in both infrared and Raman spectra, while the A_1 Raman band will be surprisingly weak.⁸ The F_2 Raman band will be depolarized (dp) but the A_1 band will be highly polarized (p).

In a contact ion pair, the Na^+ will have a pronounced effect upon the $\text{Co}(\text{CO})_4^-$ ion. When this interaction is monodentate or tridentate, a cylindrical axial field is introduced and the symmetry is C_{3v} . As a result, the degeneracy of the F_2 frequency is partially lifted to produce in its place a doubly degenerate E frequency and a nondegenerate A_1 frequency. The former can be expected to produce a strong infrared band and a strong, depolarized Raman band. The latter can be anticipated in the infrared spectrum as a band of medium intensity and in the Raman spectrum as a medium-intense band which is polarized (see, however, the discussion below). In addition to these, one will have an A_1 frequency which is closely related (similar atom displacements, etc.) to the A_1 frequency of the T_d case. It will appear as a weak, polarized Raman band at or near the position of the corresponding A_1 frequency for the T_d case. Any intensity which this frequency shows in the infrared spectrum arises from the difference between the unique CO group and the other three which is induced by the Na^+ . As a consequence it will yield a weak infrared band.

It is also possible that a contact ion pair might be formed as a result of a bidentate interaction of the Na^+ ion with the anion. In this case, the symmetry is C_{2v} and the degeneracy of the T_d F_2 frequency is completely lifted to give three well-spaced infrared bands of medium intensity ($A_1 + B_1 + B_2$). These vibrations would be expected also to give three Raman bands of medium intensity, one of which, the A_1 , would be polarized. In addition, there would be another A_1

(8) W. F. Edgell and J. Lyford, IV, *ibid.*, **52**, 4329 (1970).

vibration which would appear near the T_d A_1 frequency as a weak infrared band and a weak, polarized Raman band. These results are summarized in Figure 9.

The case of the triple ion in which two anions are in intimate contact with one Na^+ is an interesting case not only for its solution properties but also from a theoretical point of view. We consider only the case where the interaction is monodentate and assume that Na^+ produces the same cylindrical symmetry in each anion that is found in the contact ion pair and that each anion is equivalent in that each feels the same force when distorted in an equivalent manner. The vibration of one anion in the triple ion may be viewed as being coupled with the same vibration in the other anion, producing two vibrations, one in which the motions of the two anions are in phase with one another and the other in which they are out of phase. The CO stretching vibrations of this triple ion may be classified in terms of the local symmetry of the motion (A_1 or E) and in terms of the phase relation of the motion in the two anions ($a_1 =$ in phase or $a_2 =$ out of phase). For example, a vibration of symmetry type $A_1 a_2$ has local symmetry A_1 , while the two anions move out of phase. As a result of the coupling, each frequency of the monodentate contact ion pair (symmetry C_{3v}) gives rise to two frequencies in the triple ion. The complete set of CO stretching frequencies for this triple ion and their symmetry types are shown in column 3 of Figure 9. As can be seen, six frequencies are expected, two of which ($E a_1$ and $E a_2$) are doubly degenerate.

The selection rules for these frequencies will depend upon the spatial orientation of the two anions relative to each other. The rules listed in Figure 9 are for the likely case that the anions are on opposite sides of the Na^+ ion. Then the number of infrared bands and their relative intensities anticipated for the triple ion is the same as for the contact ion pair. The same is true for Raman bands. The difference between the two cases lies in the fact that the frequency of each infrared band coincides with that of a Raman band for the contact ion pair, while no coincidences occur between infrared and Raman bands for this triple ion. In the event, however, that the anions as described above are not on opposite sides of the Na^+ , all six frequencies become active in both infrared and Raman spectra.

We have seen that a free anion, symmetrically solvated, gives expectations based on T_d symmetry. This same near-neighbor environment for the $\text{Co}(\text{CO})_4^-$ ion can also occur for the solvent-separated ion pair. In such a situation, all the evidence to date indicates that the disturbance of the anion by the Na^+ is muted and the expectations are also those for T_d symmetry. One other possibility will be considered here. When solvent molecules interact strongly enough with the $\text{Co}(\text{CO})_4^-$ ion that their contribution to the forces resisting the displacement of the atoms in the vibration are not negligible, the T_d symmetry will not apply for the free anion if it is solvated unsymmetrically. If three CO groups were different from the fourth, the C_{3v} symmetry expectation would apply; if two, C_{2v} .

We are now in a position to evaluate the information in Table I. It is seen that the infrared data for the $\text{Co}(\text{CO})_4^-$ environment of kind I correspond to the anion in a T_d situation. The infrared data for the kind II environment satisfy the expectations for both a C_{3v} and a

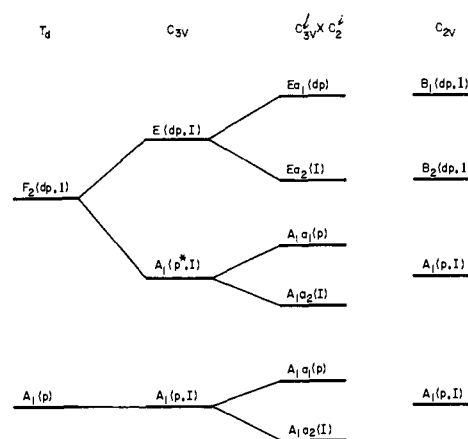
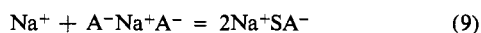
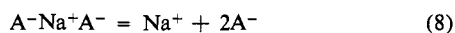
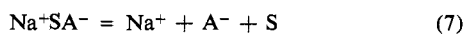
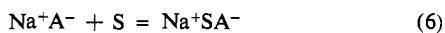
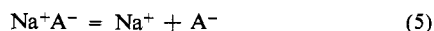


Figure 9. Schematic representation of the CO stretching frequencies expected for the $\text{Co}(\text{CO})_4^-$ ion in several types of solution sites (also see text).

$C_{3v}^i \times C_s^i$ condition. Since the differences between the frequencies of the corresponding infrared and Raman band components are small and within the uncertainties in their values, these data best satisfy the criteria for a C_{3v} condition. The assignment of the observed band components to the allowed frequencies on this basis is made in Table I. Two points deserve comment. The first has to do with the relative intensities of the A_1 and E infrared band components at 1855 and 1898 cm^{-1} , respectively. If one takes a rough model the anion with four equivalent CO groups and the same vibrational motions as in the T_d condition, one would find the intensity of the A_1 band to be half that of the E band. As the data of Table II show, this intensity ratio is close to that which is observed. This consideration was then basis for the assignment of Table I. The second point has to do with the depolarization ratios for the Raman band components. As can be seen, the expectation that depolarized bands would yield an intensity ratio in the polarization measurement of $\rho = 0.75$ and that for polarized bands $\rho < 0.75$ is satisfied for all but the A_1 band at 1855 cm^{-1} . It is shown in the Appendix, however, that a value of ρ near 0.75 is expected for this mode in the rather special case here. It results from the form of the mode of vibration and the fact that both the structural units off the C_3 axis and that on the C_3 axis are the same, *i.e.*, CO groups.

One concludes that the data of Table I are consistent with the anion in a kind I environment being in a free-ion site or a solvent-separated-ion-pair site, while the anion in a kind II environment may be in a monodentate or tridentate contact-ion-pair site or in a free-ion site with a significant unsymmetrical solvation. Further, in a triple ion, the magnitude of the frequency difference between an infrared and Raman frequency which differ only in the phase of the motion in the two halves of the ion depends upon the extent of the coupling between the two anions. When this is small, there is a near coincidence between the Raman and infrared band. Consequently, the data of Table I for the kind II environment are also consistent with anions in triple ion sites where the anion-anion coupling is small.

Equilibria involving sites consistent with the infrared and Raman spectra include



In these equations, A^- stands for the symmetrically solvated anion; S stands for solvent; SA^- stands for the unsymmetrically solvated anion; and Na^+ , Na^+A^- , and Na^+SA^- stand for the cation, contact ion pair, and solvent-separated ion pair, all solvated, of course. Since the variation of the population of the different anion sites with gross salt concentration depends upon the equilibria involved, the relationship between them serves as a means of identification of the sites present. Because the integrated absorbance E of the infrared band arising from a vibration of the anion in a particular site is proportional to that site concentration, its variation with salt concentration may be examined for this purpose. Suppose that kind I and kind II environments were the solution structures A^- and Na^+A^- . Then the equilibrium expressed by eq 5 would require that the ratio of the population of these two environments be a function of the gross salt concentration. This, in turn, would require that E_I/E_{II} and E_{III}/E_{II} be functions of gross salt concentration. The data of Figure 5 show that this is not the case, and such an identification is not possible. In the same way, equilibrium 8 may be eliminated as a dominant factor. These concentration data (plus those of Table I) are consistent with either equilibrium 4 or 6 or 9. However, note that the presence in substantial amounts of the pair of ion sites A^- , SA^- together in the solution with either Na^+A^- , Na^+SA^- or Na^+SA^- , $A^-Na^+A^-$ in major quantities is inconsistent with the elimination of equilibria 5 and 8. Note also that the postulate that (7) is the equilibrium between the sites in major amounts is not in agreement with the facts of Table I.

Thus, (4) or (6) or (9) may be the major equilibrium as far as the spectroscopic data may be interpreted at present. A resolution between them may be made on the basis of electrical conductivity.

The equivalent conductance of $NaCo(CO)_4$ in THF solutions has been measured.^{4,9} The values of λ vary from 9 to 16 ohm^{-1} over the concentration range of this study. The equivalent conductance of the Na^+ at infinite dilution in THF is 48 ohm^{-1} , while those for a number of aromatic radical anions range from 47 to 80 in THF, as measured by Szwarc and coworkers.¹⁰ The value of λ_0 for $NaCo(CO)_4$ in THF may be estimated roughly as 100 ohm^{-1} from these results. These values of λ and λ_0 for the carbonylate salt are not consistent with the major anion sites in solution being those of equilibrium 4 or 9, but are what one would expect for equilibrium 6.

Summing up the various findings, this study shows that the $Co(CO)_4^-$ ion is in two kinds of environment in these solutions and that a major portion of the anions in one kind of environment is in contact-ion-pair sites, while the major portion in the other kind is in solvent-

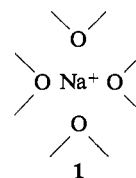
(9) More recently, Mr. J. Fisher repeated these measurements in this laboratory with nearly the same results.

(10) D. Bhattacharyya, C. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965); R. Slaters and M. Szwarc, *ibid.*, **69**, 4124 (1965).

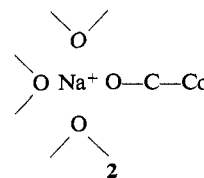
separated-ion-pair sites. This does not preclude the presence of other anion sites. For example, the equivalent conductance values require the presence of some free ions. And the form of λ vs. \sqrt{c} curve⁴ implies the presence of some triple ions in the higher concentration range of this study. Moreover, more than one kind of contact ion pair can exist. These results are in harmony with other work. Far-infrared spectra of sodium salts in THF show that the frequency of the Na^+ vibration is dependent upon the anion, which leads to the conclusion that the Na^+ vibrates in a cage formed by the solvated contact ion pair.^{11,12} Extensive work by Szwarc and coworkers¹³ and by Hogen-Esch and Smid¹⁴ has established the presence of contact ion pairs and solvent-separated ion pairs for alkali salts of carbanions in THF.

The present work provides evidence pertaining to the structure of the contact ion pair. As indicated in the Appendix, the deformation of the unique CO group in the A_1 vibration of the 1890- cm^{-1} complex is about three times as great as that of each of the other three CO groups. In the E vibrations, the unique CO group does not participate. Since the effect of the Na^+ is to weaken the C-O bond in the groups it touches in the contact ion pair, the vibrations which involve more deformation of the contacted CO groups will be lower in frequency. As discussed above (see Table I), 1855 cm^{-1} is assigned to the A_1 vibration in question, while the E modes are found at 1898 cm^{-1} . It follows that the unique CO group has the weakest bond and that the contact interaction is monodentate.

A major goal of this work was to learn something about the cation sites in this solution using the vibrations of the anion as a probe. The results show that the major cation sites are the cation surrounded by solvent molecules in the solvent-separated ion pair, whose near-neighbor environment may be indicated schematically as 1, and the cation in the contact ion pair, whose



near-neighbor environment may be shown schematically by replacing one of the solvent molecules by the $Co(CO)_4^-$ anion, *i.e.*, 2. Only one broad band which is



associated with the vibration of the Na^+ , and whose integrated absorbance is proportional to gross salt con-

(11) W. F. Edgell and A. T. Watts, Abstracts, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1965, p 85; W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. Risen, Jr., *J. Amer. Chem. Soc.*, **88**, 1815 (1966).

(12) W. F. Edgell, J. Lyford, IV, R. Wright, W. Risen, Jr., and A. T. Watts, *ibid.*, **92**, 2240 (1970).

(13) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes," Interscience, New York, N. Y., 1968, and references cited therein.

(14) T. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307, 318 (1966).

centration, is found in the far-infrared spectrum of $\text{NaCo}(\text{CO})_4$ in THF.^{11,12} Although this band could be assigned to the vibration of the Na^+ in either the solvent-separated ion pair site or the contact ion pair site, since the concentration of the anion in either site is shown above to be proportional to salt concentration, it seems far preferable to believe that the one band comes from the vibration of the Na^+ ion in both (or all) cation sites. Support for such a view comes from the fact that Na^+ ion also gives a strong (and broad) far-infrared band when it is in a solvent in which its near-neighbor environment consists only of solvent molecules, as shown by work in this laboratory¹² and by Popov and co-workers.¹⁵ Further, the cage in which the Na^+ vibrates in this THF solution is very similar in both sites, as can be seen from the above diagrams. This will cause the frequency of vibration in both sites to be nearly the same, since it has been shown that the repulsion terms in the expression for the energy of the system make the principal contribution to the net force constant for the vibration of alkali ions in solution.¹²

Let us turn now to a consideration of the thermodynamic results of Table IV and Figure 7. With the identification of the anion sites, it is seen that these data apply to the conversion of contact ion pairs to solvent-separated ion pairs, for which $\Delta H = -3.7$ kcal/mol is found for $\text{NaCo}(\text{CO})_4$ in THF. This value is lower than that obtained for the same equilibrium for two other sodium salts in THF, using different techniques. Hogen-Esch and Smid¹⁴ find -7.6 for sodium fluorenyl, while Grutzner, Lawlor, and Jackman¹⁶ obtain -8.2 for sodium triphenylmethanide and -6.7 for sodium fluorenyl. These latter compounds are salts of large carbanions, and the differences in the ΔH values might be sought in that fact.

The heat effect in the conversion of contact ion pairs into solvent-separated ion pairs may be obtained as the difference between the heat required to dissociate each species, *i.e.*, between processes 5 and 7. Some success has been obtained in dealing with such a dissociation in terms of the Denison-Ramsey equation¹⁷

$$\Delta H_{\text{diss}} = (Ne^2/rD)(1 + d \ln D/d \ln T)$$

and it is tempting to rationalize the values of ΔH for the ion-pair conversion process in terms of an equation obtained from that above by replacing the $1/r$ term by the difference in $1/r$ values for the contact ion pair and the solvent-separated ion pair. However, expressions for the potential energy of an ion pair with the dielectric constant D in the denominator fail badly in accounting for the vibrational frequencies of the alkali ions in solution¹² and hence do not give a satisfactory account of the short-range forces. And an examination of structures 1 and 2 shows that the differences in the short-range forces are the essence of the ion-pair conversion process.

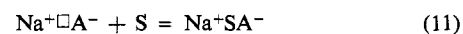
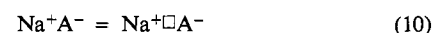
It was found that potential energy expressions which replaced the dielectric constant shortcut by summing the coulombic interactions of the ions with the charge centers of the near-neighbor solvent molecules can give calculated net force constants for alkali ion vibrations in solution in good agreement with experimentally derived

(15) B. Maxey and A. Popov, *J. Amer. Chem. Soc.*, **89**, 2230 (1967); **91**, 20 (1969); J. Wuepper and A. Popov, *ibid.*, **91**, 4352 (1969); **92**, 1493 (1970).

(16) J. Grutzner, J. Lawlor, and L. Jackman, *ibid.*, in press.

(17) J. Denison and J. Ramsey, *ibid.*, **77**, 2615 (1955).

values.¹² If one compares this kind of expression for the two kinds of ion pairs, it becomes apparent that it is useful to consider the conversion process as being divided into two steps



In the first step, the cation and anion are moved apart in the solution to their position in the solvent-separated ion pair, creating a hole between them. Solvent fills this hole in the second step. The enthalpy change involved in the second step is negative and is dominated by the interaction of the added solvent molecules¹⁸ with cation. Small (negative) terms also come from the interaction of the added solvent molecules with the anion and small (positive) terms from the desolvation of the added solvent molecules. As long as the same number of solvent molecules are added in the conversion process, the enthalpy change for this step will show little variation with anion, but it will increase substantially with each additional solvent molecule added to the near-neighbor shell of the cation. The enthalpy change in the first step is positive and arises from separating the coulombic charges of the cation and its near-neighbor solvent molecules from those of the anion and its near-neighbor environment from the contact pair positions to the solvent-separated pair positions, plus that involved in pushing back the solvent to make the hole. This latter contribution should be nearly the same in two conversion processes in the same solvent if the same number of solvent molecules are added to the contact pair to form the solvent-separated pair. In that case, any substantial difference in ΔH for the first step would arise from the charge-separation process and would be more positive the more the anion charge is concentrated near the cation in the contact ion pair.

One can now offer a possible explanation for the difference in ΔH for the ion pair conversion process in THF between $\text{NaCo}(\text{CO})_4$, on the one hand, and the sodium salts of the carbanions, on the other. The charge of the anion is more diffuse for the carbanions, and this will result in making ΔH for the conversion process involving the carbanions more negative by making the enthalpy change in the first step, eq 10, less positive than for the process with the $\text{Co}(\text{CO})_4^-$ ion. A similar explanation has offered by Grutzner, *et al.*,¹⁶ for the differences in ΔH among the several anions studied by them. In light of the finding in this study that the attachment of the Na^+ to the $\text{Co}(\text{CO})_4^-$ is monodentate, one expects one THF molecule to be displaced from the cation near-neighbor shell on forming the contact ion pair from the solvent-separated pair; see structures 1 and 2. However, the above carbanions are large and flat, and it is just possible that they might displace two solvent molecules from the cation near-neighbor shell in the conversion to the contact ion pair to contribute to the observed ΔH difference.

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(18) The plural is used here for generality, but it is anticipated that one solvent molecule will most often be involved.

and Charles Allemand (Jarrell-Ash) for Raman measurements.

Appendix

The changes in the properties of the $\text{Co}(\text{CO})_4^-$ ion produced by changing its environment in solution from that which produces the T_d spectra to that which gives the C_{3v} spectra are expected to be small compared with the values for the properties dictated by the internal structure of the ion. Thus, one would expect the atom displacements in each vibration of the C_{3v} anion to be nearly the same as those of the corresponding mode of the T_d anion. An acceptable set of relative changes in the CO bond lengths is given in Table V, wherein N is

Table V. Relative Distortions of the CO Groups of the $\text{Co}(\text{CO})_4^-$ Ion in Environments Which Produce T_d and C_{3v} Symmetry

---Vibration---		ΔR_1	ΔR_2	ΔR_3	ΔR_4	N
T_d	C_{3v}					
A_1	A_1 mode 1	1	1	1	1	1/2
F_2 mode 1	A_1 mode 2	3	-1	-1	-1	$1/\sqrt{12}$
F_2 mode 2	E mode 1		1	-1		$1/\sqrt{2}$
F_2 mode 3	E mode 2		1	1	-2	$1/\sqrt{6}$

the normalization constant required to reduce the kinetic and potential energy in each mode to the same value and the subscript 1 refers to the unique CO group. The integrated intensity of a vibration in the infrared spectrum is given by

$$B = CN^2 \left| \sum_g \mathbf{u}_g \Delta R_g \right|^2$$

where C is a constant, the sum is over the CO groups, and the bond dipole moment assumption has been introduced for simplicity. With the deformations of

Table V and the geometry of the tetrahedral ion, one obtains

$$A_1 \text{ mode 2} \quad B_{A_1} = (3\mu' + \mu)^2 C/12$$

$$E \text{ mode 1 or 2} \quad B = 4\mu^2 C/3$$

where μ' is the dipole produced in the unique CO group by a unit distortion of the bond, and μ is the same for each of the other CO groups. Since E mode 1 and mode 2 are degenerate, the observed intensity B_E is the sum of that for the two modes. In light of the above discussion of ion properties, $\mu' \approx \mu$, from which

$$B_{A_1} \approx B_E/2$$

Let us turn now to a consideration of the depolarization ratio ρ for the A_1 mode 2 vibration. For the way in which the experiment was carried out

$$\rho = 3\beta^2/(45\alpha^2 + 4\beta^2)$$

where β is the anisotropy and α the spherical part of the polarizability tensor. Because α is zero by symmetry for the E modes, $\rho = 3/4$; since α does not vanish by symmetry for A_1 modes, ρ is $< 3/4$ —the value for stretching vibrations usually being < 0.2 . By dividing the molecular polarizability into contributions from each CO group, as was done above for the dipole moment, one obtains for the A_1 mode 2 vibration

$$\alpha = 3\{(\alpha_a' + 2\alpha_p') - (\alpha_a + 2\alpha_p)\}$$

where α_a' and α_p' are the changes in the axial and perpendicular polarizabilities of the unique CO group produced by a unit distortion of the bond and α_a and α_p are the same quantities for each of the other CO groups. Now, expecting $\alpha_a' \approx \alpha_a$ and $\alpha_p' \approx \alpha_p$, one finds

$$\alpha \approx 0, \rho \approx 3/4$$

for this A_1 vibration.