

stepwise process for constructing the background intensity function,  $B_n(s) \simeq I_b(s)$  in  $n$  steps.

An initial smooth background line is obtained by using null points from a molecular intensity function computed from a model of the structure and fitting the functions  $b_p(s)$  to a sequence of segments, each containing three points of the total intensity curve coincident with alternate null points. The molecular intensity function  $I_m(s)$  is obtained in the usual manner from the total intensity function  $I_t(s)$  using<sup>5</sup>

$$I_m(s) = (I_t(s)/I_b(s)) - 1 \quad (\text{A3})$$

The radial distribution function  $f(r)$

$$f(r) = (2/\pi)^{1/2} \int_0^{s_{\max}} s I_m(s) \exp(-as^2) \sin sr ds \quad (\text{A4})$$

is made positive by attaching "Gaussian tails" to the edges of the significant nonzero peaks. A Gaussian

function is fitted by least squares to the lower 5–10% of the peak edge. The function is then smoothly averaged with the lower 2–5% of the peak edge and used as the extension of the peak in the region where it should have small values. The entire radial distribution function is made positive in this manner and then transformed to yield the next approximate molecular intensity function, which is used to generate new points for an improved background intensity function. The improved  $I_b(s)$  is obtained from eq A3 using the  $I_m(s)$  obtained from the "positivized" radial distribution curve. Many values of the new  $I_b(s)$  may now be employed with a least-squares calculation to fit the functions  $b_p(s)$ , eq A1, to  $I_b(s)$  in several overlapping ranges of  $s$ . A new composite background intensity function is then derived from the process described by eq A2. Further recycling ultimately produces a smooth background intensity function  $I_b(s)$  which generates an essentially positive radial distribution curve obeying the area criterion.<sup>5</sup>

## Studies of Some Aspects of Solution Character by Molecular Spectroscopy. IV. On the Multiplicity and Nature of the $\text{Co}(\text{CO})_4^-$ Environments in Certain Solvents<sup>1,2</sup>

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**Abstract:** The infrared band near  $1900 \text{ cm}^{-1}$  was examined for  $\text{NaCo}(\text{CO})_4$  in eight solvent systems. The band envelope was found to be simple for DMF, DMSO, and wet THF, but showed varying degrees of complexity for pyridine, piperidine, THF, and DME. Water is sufficiently different to be considered a special case. The results are discussed in terms of the differing multiplicities and differing nature of the anion environment. A band component near  $1887 \text{ cm}^{-1}$  is found in all solutions but water (and perhaps piperidine), and it is associated with the internal vibration of the anion in a symmetrical "solvent-surrounded" ion environment. Band components above and below this frequency are associated with the anion in asymmetrical solution environments.

The discovery that alkali ions vibrate in solution offers an opportunity to investigate the dynamics, forces, and structure in solutions near ions.<sup>1b</sup> A more complete understanding of the vibration of an alkali ion is obtained if one has an understanding of its immediate surrounding in the solution. It has been found that a single broad infrared band is observed for this vibration in virtually all of the solutions examined to date.<sup>1b,c,4-8</sup>

These cases cover a variety of salts and solvents. Does this mean that the alkali ion is found in only one environment in these solutions? This question is investigated in this study.

The intramolecular vibrations of a polyatomic ion reflect its immediate surroundings. Hence, the internal vibrations of a polyatomic anion in solution serve as a probe of the anion environment and, *mutatis mutandis*, of that of the cation. The tetracarbonylcobaltate ion,  $\text{Co}(\text{CO})_4^-$ , was chosen as an anionic probe of the ion environments for this study because its salts are soluble in a variety of solvents. Moreover, the C–O stretching frequencies near  $1900 \text{ cm}^{-1}$  are sensitive to environment. The solvents chosen cover a wide range of solution properties, while the differences between  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  salts were examined in a single solvent of intermediate character.

### Experimental Section

The infrared measurements were made in the  $1900\text{-cm}^{-1}$  region with a Perkin-Elmer spectrophotometer, Model 421. Cells with  $\text{CaF}_2$  or  $\text{KBr}$  windows were used. The solvents used in this study

(1) (a) Part I: W. F. Edgell, M. T. Yang, and M. Koizumi, *J. Amer. Chem. Soc.*, **87**, 2563 (1965). (b) Part II: 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). (c) Part III: W. F. Edgell, J. Lyford, IV, R. Wright, W. Risen, Jr., and A. T. Watts, *ibid.*, **92**, 2240 (1970).

(2) Based in part upon the Ph.D. theses of J. Lyford, IV, June 1969, and of A. Barbetta, in preparation.

(3) On leave from the National Chemical Laboratory, Poona, India.

(4) B. W. Maxey and A. I. Popov, *J. Amer. Chem. Soc.*, **89**, 2230 (1967).

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(6) J. L. Wuepper and A. I. Popov, *ibid.*, **91**, 4352 (1969); **92**, 1493 (1970).

(7) W. Risen, private communications.

(8) M. J. French and J. L. Wood, *J. Chem. Phys.*, **49**, 2358 (1968).

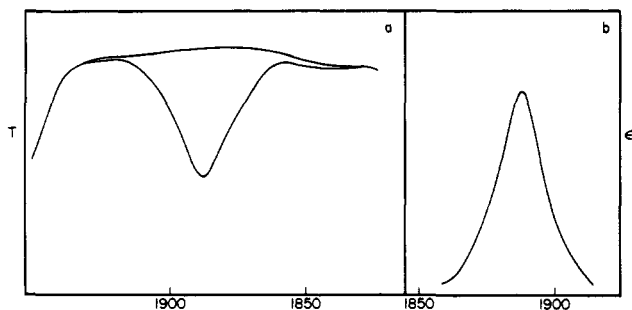


Figure 1. (a) Infrared spectrum of  $\text{NaCo}(\text{CO})_4$  in DMF: upper curve, solvent transmission; lower curve, solution transmission. Fiduciary marks are 1850 and  $1900\text{ cm}^{-1}$ . (b) Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in DMF. Fiduciary marks are 1850 and  $1900\text{ cm}^{-1}$ .

absorb to a greater or lesser extent in the  $1900\text{-cm}^{-1}$  region. To eliminate absorption due to the solvent molecules at each wavelength of the solute band, spectra of both the pure solvent and the solution in the same cell in the sample beam were obtained. Care was exercised to maintain conditions so that both solvent and solutions traced an identical curve outside the region of solvent absorption. An example of such curves is shown for  $\text{NaCo}(\text{CO})_4$  dissolved in DMF in Figure 1a. An extinction coefficient of the solute in solution was computed at each wavelength from each such pair of curves by the equation  $\epsilon^{-1}c^{-1} \ln(T_0/T)$ , where  $T_0$  is the transmission of the pure solvent and  $T$  is that of the solution at the wavelength,  $c$  is the concentration, and  $t$  is the cell thickness. Figure 1b shows the extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in DMF obtained from the curves of Figure 1a.

The  $\text{Co}(\text{CO})_4^-$  ion is very oxygen sensitive. Moreover, traces of water would be expected, *a posteriori*, to alter ion environments in the dilute solutions used for these studies. Consequently, efforts were made to maintain anaerobic and dry conditions. All manipulations were carried out under dry nitrogen or on a vacuum line, and all solvents were dried and deaerated before use. The tetrahydrofuran (THF) and dimethoxyethane (DME) were dried and deoxygenated by a sequential procedure involving storage over Na ribbon, distillation in a stream of dry  $\text{N}_2$ , deaeration on a vacuum line, and distillation *in vacuo* onto newly activated Linde 4A molecular sieves. Dimethylformamide (DMF), pyridine, and piperidine were stored over  $\text{CaH}_2$  and then subjected to the same purification steps used for THF and DME after the storage over Na step. Dimethyl sulfoxide (DMSO) was placed directly onto molecular sieves and then deaerated; distilled water was subject only to deaeration.

The white salts,  $\text{NaCo}(\text{CO})_4$  and  $\text{KCo}(\text{CO})_4$ , were prepared as described elsewhere.<sup>9</sup> Solutions of these salts were made by dissolving the salts in the dry solvents. The solutions of  $\text{LiCo}(\text{CO})_4$  were prepared by mixing stoichiometric amounts of  $\text{LiCl}$  and  $\text{NaCo}(\text{CO})_4$  dissolved in THF and then filtering off the insoluble  $\text{NaCl}$ . Concentrations were determined by analyzing for Co spectrophotometrically by the nitroso-R method.

## Results and Discussion

The geometry of an isolated  $\text{Co}(\text{CO})_4^-$  ion would be expected to be tetrahedral. Such an ion would give rise<sup>10</sup> to a triply degenerate, infrared-active C–O stretching frequency near  $1900\text{ cm}^{-1}$ . When this ion exists in a solution environment whose forces on the ion, when it vibrates, do not effectively modify the tetrahedral character of the symmetry, again one triply degenerate frequency will be found.<sup>11</sup> However, if these forces lack this symmetry, all or part of the degeneracy is lifted, and the band may be split into two or three components depending upon the symmetry of the significant environmental forces as discussed in the following paper.

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

(10) W. F. Edgell and J. Lyford, IV, *J. Chem. Phys.*, **52**, 4329 (1970).

(11) Note that this does not necessarily require that the molecular arrangement in the near neighborhood of the  $\text{Co}(\text{CO})_4^-$  ion show tetrahedral symmetry.

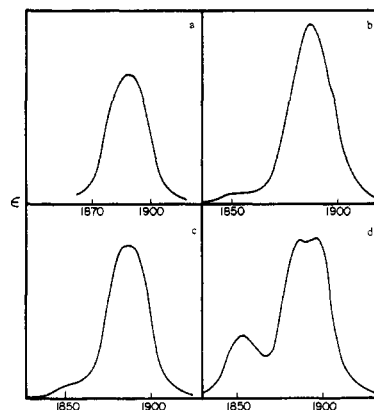


Figure 2. (a) Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in DMSO. Fiduciary marks are 1870 and  $1900\text{ cm}^{-1}$ . (b) Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in DME. Fiduciary marks are 1850 and  $1900\text{ cm}^{-1}$ . (c) Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in pyridine. Fiduciary marks are 1850 and  $1900\text{ cm}^{-1}$ . (d) Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in THF. Fiduciary marks are 1850 and  $1900\text{ cm}^{-1}$ .

Hence we looked for environmental multiplicity by examining the shape of the infrared band envelope near  $1900\text{ cm}^{-1}$ .

In the first series of experiments, this region of the infrared spectrum was examined for  $\text{NaCo}(\text{CO})_4$  in a series of solvents. Figure 1b shows the extinction coefficient curve for this salt in DMF. A single band is observed, and this indicates that the effective forces at the anion in this solution are symmetrical and essentially the same at each anion. Two kinds of solution structure can give this result, "free" anions and a solvent-separated ion pair. The assumption in the second case is that the solvent separating the cation and anion mutes the field of the former upon the latter—an assumption which seems justified by the data obtained to date. In both these solution structures, the anion (and the cation) sees only solvent molecules in its near-neighbor shell. Since both these cases are expected to yield a similar band shape, both cases (or a mixture of them) are designated by the phrase solvent-surrounded ions.

Similar results are obtained with DMSO, as can be seen in Figure 2a. Although there is a hint of a small amount of a second environment in the shape of the curve in the  $1850\text{-cm}^{-1}$  region, the overwhelming part of the absorption corresponds to a single band, which indicates a solvent surrounded anion. This, in turn, implies that the environmental situation at the cation is the solvent-surrounded cation.

If one examines this spectral region for  $\text{NaCo}(\text{CO})_4$  solutions in which DME, pyridine, and THF are the solvents, one obtains the results shown in Figures 2b–d. All bands are complex. In addition to the main absorption component at about  $1887\text{ cm}^{-1}$ , each band shows a well-separated absorption component near  $1855\text{ cm}^{-1}$  and each band gives indication of the presence of an absorption component slightly above  $1887\text{ cm}^{-1}$ . In the case of the THF solutions, both the high-frequency component at about  $1895\text{ cm}^{-1}$  and the low-frequency component near  $1855\text{ cm}^{-1}$  lose intensity when one adds water to the solution, while the  $1889\text{-cm}^{-1}$  component gains intensity. And it will be shown in the following paper that the same thing occurs when the temperature of the solution is lowered. These results show that the

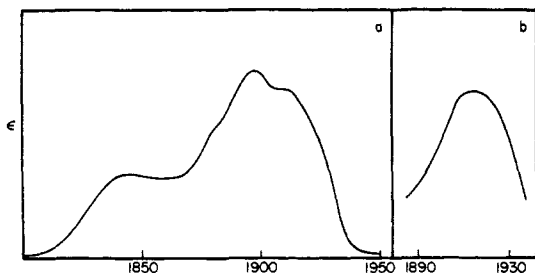


Figure 3. (a) Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in piperidine. Fiduciary marks are 1850 and 1900  $\text{cm}^{-1}$ . (b) Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in water. Fiduciary marks are 1890 and 1930  $\text{cm}^{-1}$ .

1887- $\text{cm}^{-1}$  component arises from the  $\text{Co}(\text{CO})_4^-$  in a different environment from that for those anions which generate the 1895- $\text{cm}^{-1}$  component. They further imply that both the 1855- and 1895- $\text{cm}^{-1}$  absorption components arise from vibrations of the  $\text{Co}(\text{CO})_4^-$  ion in the same environment. It is reasonable to make a similar assignment of band components for the DME and pyridine solutions. Thus one can conclude that there are (at least) two near-neighbor environments for the  $\text{Co}(\text{CO})_4^-$  ion in the THF, DME, and pyridine solutions of  $\text{NaCo}(\text{CO})_4$ . This suggests that there are also (at least) two environments for the  $\text{Na}^+$  ion in these solutions.

Figure 3a shows the spectrum of  $\text{NaCo}(\text{CO})_4$  in piperidine solution. The band envelope is more complex than that for the THF solution. Clearly the set or the mix of anion environments in the piperidine solution differs from that in the THF solution. There are at least two—and quite likely more—anion environments for  $\text{NaCo}(\text{CO})_4$  in piperidine.

It would be desirable to have similar information for this salt in water. Fortunately, there is an infrared "window" in water at this wavelength region and Figure 3b shows the result. The band is so broad that it reminds one of the vibration of a hydrogen bond. Many anion environments apparently exist in the water solution and the situation is in a different class from that of the other solvents.

The question naturally arises about the solution structures for other alkali salts of the  $\text{Co}(\text{CO})_4^-$  ion in a variety of solvents and how they compare with the  $\text{Na}^+$  salt solutions. One can get a good answer to this question by comparing the results for the salts of the more common alkali ions  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  in a solvent which shows intermediate complexity for the  $\text{Na}^+$  salt. This would leave room for noticeable change in either direction. THF is such a solvent, and Figures 4a and 4b give the extinction coefficient curve of the  $\text{Li}^+$  and  $\text{K}^+$  salt in it. Like the  $\text{NaCo}(\text{CO})_4$  solution, these solutions also show the presence of two (or more) solution structures at the anion.

It is possible to draw some further conclusions about the solution structures at the ions from these results. The single band which occurs in DMF at 1888  $\text{cm}^{-1}$  has been attributed to the solvent-surrounded anion. Bands or component bands occur at essentially this same frequency for the  $\text{NaCo}(\text{CO})_4$  solution with DMSO, DME, THF, and pyridine as solvents and for  $\text{LiCo}(\text{CO})_4$  and  $\text{KCo}(\text{CO})_4$  in THF. Because this band component appears at nearly the same frequency in each of these

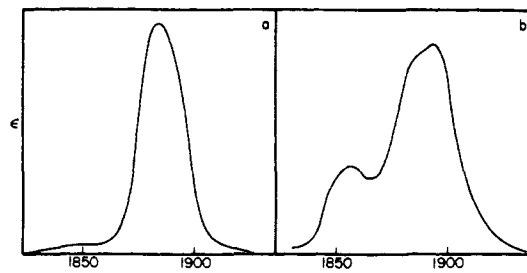


Figure 4. (a) Extinction coefficient curve for  $\text{LiCo}(\text{CO})_4$  in THF. Fiduciary marks are 1850 and 1900  $\text{cm}^{-1}$ . (b) Extinction coefficient curve for  $\text{KCo}(\text{CO})_4$  in THF. Fiduciary marks are 1850 and 1900  $\text{cm}^{-1}$ .

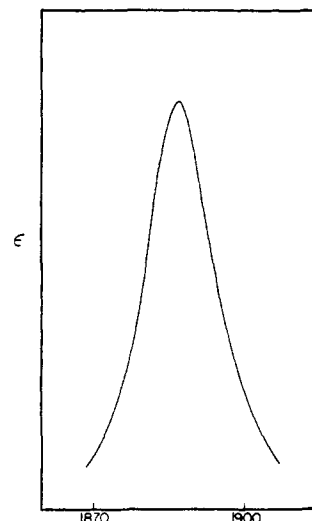


Figure 5. Extinction coefficient curve for  $\text{NaCo}(\text{CO})_4$  in wet THF (5%  $\text{H}_2\text{O}$ ). Fiduciary marks are 1870 and 1900  $\text{cm}^{-1}$ .

solutions, it is concluded that it also arises from the  $\text{Co}(\text{CO})_4^-$  ion in a solvent-surrounded environment in each of these solutions. This implies that in this solution-structure situation the solvent molecules solvate the cation keeping it away from the  $\text{Co}(\text{CO})_4^-$ , while the latter ion interacts with the solvent in a less specific or less strong way so that the effective forces involved in the internal vibration of the  $\text{Co}(\text{CO})_4^-$  ion are essentially the same in each solvent. Support for these ideas comes from the experiment of adding water to THF solutions of  $\text{NaCo}(\text{CO})_4$  mentioned above. When the amount of added water is several per cent, the spectrum shown in Figure 5 is obtained. The frequency of this single band is not that characteristic of the  $\text{Co}(\text{CO})_4^-$  ion in water (1915  $\text{cm}^{-1}$ ) but is, in fact, the value assigned to this anion in the solvent-surrounded environment, namely, 1888  $\text{cm}^{-1}$ . The explanation is that the water has solvated the  $\text{Na}^+$  and removed it from the environs of the  $\text{Co}(\text{CO})_4^-$  ion so that the latter ion feels the effective forces characteristic of THF molecules in the near-neighbor environment. The clear difference between  $\text{NaCo}(\text{CO})_4$  in wet THF and  $\text{NaCo}(\text{CO})_4$  in water suggests that in the latter case, the water not only solvates the  $\text{Na}^+$  but also strongly interacts with the  $\text{Co}(\text{CO})_4^-$  ion, producing a change in the effective forces felt by the anion during its vibration as well as producing a variety of environments for it.

However, the essentially tetrahedral solvent-surrounded anion is not the only environment in which the

$\text{Co}(\text{CO})_4^-$  ion exists in the THF, DME, and pyridine solutions. The fact that two regions of absorption (those located above and below the  $1887\text{-cm}^{-1}$  component) are associated with the  $\text{Co}(\text{CO})_4^-$  ion in such a condition shows that its near-neighbor surroundings are unsymmetrical in such a solution structure. One naturally indicts the alkali ion for this lack of symmetry, but it is good to remember that the solvent can also solvate an anion so strongly that anion vibrational degeneracy is lifted. In this connection, see the work of Irish and Davis<sup>12</sup> and Davis, Macklin, and Plane<sup>13</sup> showing that the degeneracy of  $\nu_2$  of the  $\text{NO}_3^-$  ion is lifted by solvent-anion interaction in water and chloroform solutions. Some possibilities, then, for environments of this kind are: contact ion pairs, triple ions and higher clusters, and unsymmetrical solvent interaction with the anion. It is not possible to differentiate between such anion environments on the basis of the information presented here. This question, however, is taken up for  $\text{NaCo}(\text{CO})_4$  in THF in the following paper.<sup>14</sup>

One can rank the solvents in the order of their ability to produce the solvent-separated ion environments. Of the solvents tested, piperidine shows the least tendency to form the  $1888\text{-cm}^{-1}$  solvent-separated ion band, the spectrum of  $\text{NaCo}(\text{CO})_4$  in this solvent showing predominantly unsymmetrical environments for the  $\text{Co}(\text{CO})_4^-$ . THF is next in order, and here the two kinds of anion environments are more nearly equal in amounts. For DME and pyridine, all but a few per cent of the  $\text{Co}(\text{CO})_4^-$  ions are in a solvent-surrounded environment, while virtually all (spectroscopically speaking) of the anions are in this kind of a solvent environment in DMSO and DMF. The conclusions for DMSO solutions obtained above by the probe-ion technique are in agreement with the findings of Edgell, *et al.*,<sup>16</sup> and Maxey and Popov<sup>4-6</sup> that the frequency of the alkali ion vibration is independent of the anion in this solvent. McKinney and Popov have also shown that the alkali ion vibration frequency in pyridine solutions is independent of the anion.<sup>15</sup> This observation is also in harmony with the results of this work, which indicates that all but a few per cent of the ions are in solvent-surrounded environments. The small contribution to the broad infrared band of the  $\text{Na}^+$  vibration due to the cation in unsymmetric solution sites apparently is not seen. As might be expected, the probe-ion technique appears

to be more sensitive than the anion-variation method for the detection of anion environments present in modest amount.

It is possible to rationalize these results. The high donor ability of DMSO and DMF causes the virtually complete solvation of the  $\text{Na}^+$  with the resultant formation of the solvent-surrounded anion. The solvation of the  $\text{Na}^+$  is only slightly less complete when pyridine and DME are the solvents. This outcome, in the latter case, might result from the interaction of the  $\text{Na}^+$  with both oxygen atoms of the DME molecule to form a five-membered ring. In the case of THF, the donor ability of the solvent has dropped to the point that the  $\text{Co}(\text{CO})_4^-$  ion may compete with it for presence in the near-neighbor shell of the cation. Although the band envelope for the salt in piperidine shows no absorption maximum near  $1887\text{ cm}^{-1}$ , its contour suggests that a small amount of an absorption component may be present at this frequency. This implies that piperidine has an even lower donor ability than THF toward  $\text{Na}^+$ . It may be that some of the asymmetry in the anion environments in this case arise from a more specific solvation of the anion *via* hydrogen bonding.

One can also rank the alkali ions in the order of their ability to produce the spectroscopically simple environment for the anion. It is seen from Figure 4a that the vast majority of the anions are in a solvent-surrounded environment for  $\text{LiCo}(\text{CO})_4$  in THF. On the other hand, the situation for  $\text{KCo}(\text{CO})_4$  in THF is much like that of the sodium salt in the same solvent, namely, a more nearly equal mixture of symmetrical and unsymmetrical environments for the anion. This presumably means that  $\text{Li}^+$  is solvated much more strongly by THF than are the  $\text{Na}^+$  or  $\text{K}^+$  ions, an observation which was also made from ultraviolet spectral studies of alkali fluorenyls.<sup>16</sup>

It is now possible to correct earlier interpretations. Edgell, Yang, and Koizumi interpreted the three regions of absorption of the  $1900\text{-cm}^{-1}$  complex band for  $\text{NaCo}(\text{CO})_4$  in THF as arising from a single species.<sup>1a</sup> This explanation is not nearly as satisfactory as the one presented here, in view of the results cited above for adding water to the THF solutions and the effects of lowering the temperature which are discussed in the following paper.<sup>14</sup>

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(15) A. I. Popov, private communication.

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