Raman Spectral Investigation of the Interactions between Group II Cations and Ethylene Glycol in Aqueous Solutions †

By **Robert M. Williams** and **Rajai H. Atalla,*** The Institute of Paper Chemistry, Appleton, Wisconsin 54911, U.S.A.

Studies of the Raman spectra of aqueous solutions of ethylene glycol (EG) containing Group II cations revealed that calcium, zinc, and strontium ions bring about significant changes in the C–C and C–O stretching regions, while magnesium, cadmium, and barium ions result in only minor changes primarily in the C–O stretching region. These changes were compared with the effects of some of the ions on a series of related molecules including methanol and ethanol, the cyclohexane-1,2-diols, and ethylenediamine. The results indicate that the effects of calcium, zinc, or strontium ions on the spectrum of EG are most consistent with bidentate co-ordination of the metal ions and an attendant conversion of ethylene glycol from *trans-* to *gauche*-form. The minor changes arising from the presence of magnesium, cadmium, or barium ions are those expected from monodentate co-ordination. The i.r. spectra of solutions of calcium chloride in ethylene glycol reveal changes which are consistent with the interpretation of the Raman spectra.

THE formation of complexes between carbohydrates and multivalent cations has been observed in a number of different contexts.[1] Complexes with transition metal ions are reasonably understood in terms of co-ordination involving the vacant *d*-orbitals of the ions. Complexes with Group II cations are less well understood, however, and the interactions responsible have recently attracted new interest, in part because of their significance in biological systems.

The complexes of carbohydrates with divalent cations have been investigated both in solution and in the solid

---

† Based in part on a study submitted by R. M. W. to the faculty of The Institute of Paper Chemistry in partial fulfilment of the requirements for the degree of Master Science from Lawrence University, June 1973.

[1] J. A. Rendleman, 'Advances in Carbohydrate Chemistry,' Academic Press, New York, 1966, p. 209.

phase. The work of Angyal *et al.*[2,3] on solution complexes, using n.m.r. spectral measurements, indicated that three adjacent hydroxy-groups in axial-equatorial-axial configuration are prerequisite for complexation of the carbohydrate. In a study confined to zinc chloride solutions, Richards and Williams[4] found the prerequisite to be a minimum of three oxygen sites, two of which are vicinal hydroxy-groups, but without the constraint of configuration found by Angyal *et al.* The crystallographic studies of calcium complexes with a number of sugars[5-7] reveal complexation involving either two or three hydroxy-groups from each of two different sugar molecules. These suggest even fewer constraints on the structure of the carbohydrate component, though of course stability in the solid phase does not necessarily imply stability in solution. A similar reduced level of constraint for complex formation in solution is suggested, however, by the work of Thompson and his co-workers on solutions of xylans.[8,9] They developed evidence for complex formation between the xylans and some Group II cations, and in this instance it seems quite unlikely that more than two hydroxy-groups per residue can be co-ordinated to the same metal ion.

The present investigation was undertaken in an effort to clarify the prerequisites for complex formation. The approach adopted was a Raman spectral investigation of the interactions between Group II cations and ethylene glycol (EG) in aqueous solutions. For comparison purposes the effects of some of the ions on the spectra of a series of related molecules were explored. The series included methanol and ethanol, the cyclohexane-1,2-diols, and ethylenediamine (EDA). Some complementary i.r. spectral measurements on solutions in ethylene glycol were also included.

Complexes of ethylene glycol with transition metal ions were first reported by Grun *et al.*[10,11] Gomer and Tyson[12] also reported such complexes at a later date. Miyake has presented a brief discussion of the i.r. spectra of complexes of EG with cobalt(II) and nickel(II).[13] More recently Knetsch and Groeneveld[14,15] synthesized complexes of EG with salts of a number of different multivalent cations. Their analysis of the solid complexes led them to conclude that the co-ordination is bidentate for the transition metal ions, but monodentate for the Group II cations.

The Raman and i.r. spectra of liquid EG have been reported several times.[16-19] In most instances assignments of the observed bands were also made. Review of these assignments reveals disagreement concerning some of the bands. Some questions remain, particularly with respect to the rotational isomers assumed to predominate. Two erroneous arguments have been put forth and have confused interpretations of the spectra. It has been suggested that the violation of mutual exclusion among the bands in the i.r. and Raman spectra, and the presence of a permanent dipole, exclude the *trans*-form which is identified as possessing a centre of inversion as an element of symmetry. However, this argument, which is based on the symmetry of the skeleton, is valid only for the fraction of the molecules in the *trans*-conformation in which the OH bonds as well as the CO bonds are equivalent under inversion. When all possible orientations of the OH groups are considered it is clear that only two conformations possess the symmetry of point groups which include inversion as an element; when both OH groups are in the plane of the skeleton the point group is C_{2h}, and when the OH groups are on opposite sides of the skeletal plane the point group is C_i. All other conformations possess the symmetry of point group C_2, when the OH groups are on the same side of the skeletal plane, or of point group C_1, when the OH groups are not symmetrically equivalent. For these two point groups all vibrations are both i.r. and Raman active, and it is clearly not possible to rule out a permanent dipole on the basis of symmetry. These considerations are particularly relevant in the case of EG because of the significant permanent dipole of the OH group.

EXPERIMENTAL

The Raman spectra were recorded with a Spex 1401 system using a Coherent Radiation 52A argon ion laser as the exciting source. Wavelengths of exciting radiation were 514.5 or 488 nm. The 459 cm^{-1} band of carbon tetrachloride was used for calibration. Instrument slits were set for a minimum spectral resolution of 5 cm^{-1}.

All spectra were recorded in the capillary sampling mode with scattered radiation viewed at 90° to the incident beam. The capillaries were sealed to prevent evaporation losses. Most spectra were recorded twice to ascertain reproducibility of details. Scanning speeds were such that the level of detail revealed is that represented in Figure 3. Figures 1, 2, 4, and 5 were prepared from spectra recorded with contracted scales to facilitate graphic reproduction.

The i.r. spectra were recorded using a Perkin-Elmer 621 spectrometer. The cell windows were of silver bromide.

The ethylene glycol, ethanol, methanol, and ethylenediamine used were of reagent grade and were not purified further. Cyclohexanediols were obtained from Dr. L.

---

[2] S. J. Angyal and K. P. Davies, *Chem. Comm.*, 1971, 500.

[3] S. J. Angyal, *Austral. J. Chem.*, 1972, **20**, 1957.

[4] N. J. Richards and D. G. Williams, *Carbohydrate Res.*, 1970, **12**, 409.

[5] D. C. Craig, N. C. Stephenson, and J. D. Stevens, *Carbohydrate Res.*, 1972, **22**, 494.

[6] G. Richards, *Carbohydrate Res.*, 1973, **26**, 448.

[7] C. E. Bugg, *J. Amer. Chem. Soc.*, 1973, **95**, 908.

[8] B. D. E. Gaillard, N. S. Thompson, and A. J. Morak, *Carbohydrate Res.*, 1969, **11**, 509.

[9] B. D. E. Gaillard and N. S. Thompson, *Carbohydrate Res.*, 1971, **18**, 137.

[10] A. Grun and F. Bockisch, *Ber.*, 1908, **41**, 3465.

[11] A. Grun and E. Boedecker, *Ber.*, 1910, **43**, 1051.

[12] R. Gomer and G. N. Tyson, *J. Amer. Chem. Soc.*, 1944, **66**, 1331.

[13] A. Miyake, *Bull. Chem. Soc. Japan*, 1959, **32**, 1381.

[14] D. Knetsch and W. L. Groeneveld, *Inorg. Chim. Acta*, 1973, **7**, 81.

[15] D. Knetsch and W. L. Groeneveld, *Rec. Trav. chim.*, 1973, **92**, 855.

[16] K. Krishnan and R. S. Krishnan, *Proc. Indian Acad. Sci.*, 1964, **64***A*, 111.

[17] W. Sawodny, K. Niedenzu, and J. W. Dawson, *Spectrochim. Acta*, 1967, **23A**, 799.

[18] H. Matsuura and T. Miyazawa, *Bull. Chem. Soc. Japan*, 1967, **40**, 85.

[19] P. Buckley and P. A. Giguere, *Canad. J. Chem.*, 1967, **45**, 397.

Schroeder of the Institute staff, and were of better than 9% purity. All of the salts used were of reagent grade also. The water used in making up the solutions was deionized and distilled.

RESULTS AND DISCUSSION

The bands observed in the i.r. and Raman spectra of pure EG, with the exception of the O–H stretching region, are listed in Table 1. Agreement with frequencies reported in the more recent literature is quite good; there are some minor discrepancies in the number of bands observed in some of the earlier studies.

TABLE 1

Observed Raman and i.r. frequencies for glycol

Raman (cm^{-1})	I.r. (cm^{-1})
353	340
486	480
528	515
870	862
882 (shoulder)	882
1 040	1 041
1 071	
1 095	1 087
1 219	1 200
	1 250
1 275	
1 292	
	1 325
	1 360
1 406	1 405
1 466	1 450
2 728	
2 884	2 870
2 939	2 935

There are two dominant bands at 1 088 and 1 050 cm^{-1} and two distinct shoulders at 1 070 and 1 034 cm^{-1}. In contrast, the spectrum of pure EG has two bands, at 1 095 and 1 071 cm^{-1}, and a broad shoulder at 1 039 cm^{-1}. Differences in other regions of the spectra are minor.

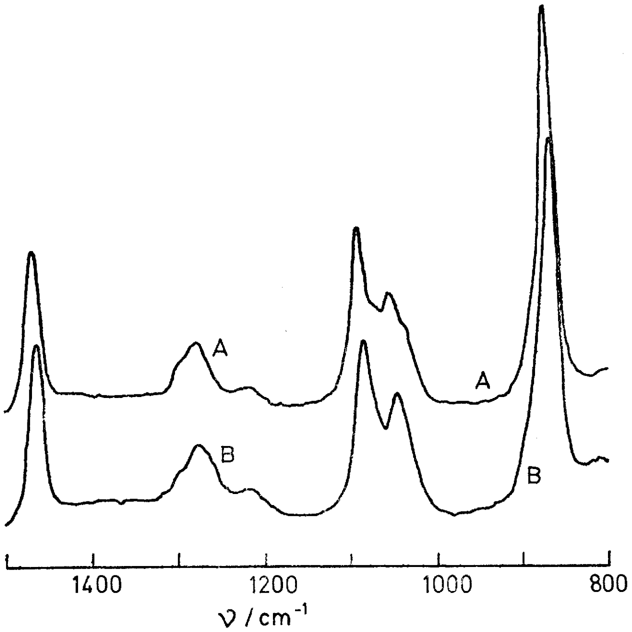

FIGURE 1 Raman spectra of the region 800—1 500 cm^{-1} for two glycol solutions: A, 5.0 mol % glycol, 95.0 mol % water; B, 5.0 mol % glycol, 88.3 mol % water, 6.7 mol % MgCl$_2$

TABLE 2

Observed Raman frequencies (cm^{-1}) for glycol–CaCl$_2$ solutions

5.0 mol % glycol 95.0 mol % water	5.0 mol % glycol 94.0 mol % water 1.0 mol % CaCl$_2$	5.0 mol % glycol 92.5 mol % water 2.5 mol % CaCl$_2$	5.0 mol % glycol 90.0 mol % water 5.0 mol % CaCl$_2$	5.0 mol % glycol 85.0 mol % water 10.0 mol % CaCl$_2$
350	348	350	354	353
485	479	484	483	478
526	522	525	531	526
866	864	866	872	870 (shoulder)
885 (shoulder)	885 (shoulder)	887	885	887
1 034	1 036			
			1 043	1 038
1 050	1 048	1 047		
1 070	1 069	1 070 (?)		
			1 081	1 075
1 088	1 086	1 085		
1 216	1 218	1 221	1 220	1 220
			1 246	1 241
1 275	1 273	1 274	1 270	
1 292	1 290	1 296	1 295	1 313
1 465	1 465	1 465	1 466	1 466
2 727	2 729	2 730	2 725	2 728
2 890	2 888	2 893	2 894	2 898
2 946	2 947	2 950	2 954	2 958

In much of the present work EG was in aqueous solution. The Raman bands observed for a 5 mol % EG solution are included in Table 2, and the 800—1 500 cm^{-1} region of the spectrum is shown as curve A in Figure 1. The EG–water spectrum has a strong, highly polarized band at 866 cm^{-1} with a shoulder at *ca.* 885 cm^{-1}. This region is very similar to that observed in the Raman spectrum of pure EG. In the EG–water spectrum, four bands are observed in the 1 000—1 100 cm^{-1} region.

Aqueous solutions of EG and several salts of Group II cations were investigated. The salts used were the chlorides of magnesium, calcium, strontium, barium, zinc, and cadmium. In order to maximize the observed effects of possible interactions, the solutions were nearly saturated in the salts. The EG concentration in all the solutions was held constant at 5 mol %.

Although changes were noted in the vibrational spectrum of EG in each of the electrolyte solutions the degree of alteration of the spectrum varied from solution to solution. Inspection of the spectra revealed that the salts could be divided into two classes according to the extent to which they altered the spectrum of EG. The chlorides of magnesium, barium, and cadmium resulted in minor changes in the 1 000—1 100 cm^{-1} region, but almost no change in other parts of the spectrum. The effect is illustrated in Figure 1 where the spectra of the EG–water system with and without added magnesium chloride can be compared. In contrast, calcium, zinc, and strontium chlorides caused extensive changes throughout the 800—1 300 cm^{-1} region. Their effects are illustrated in Figure 2 which shows the effect of added calcium chloride.

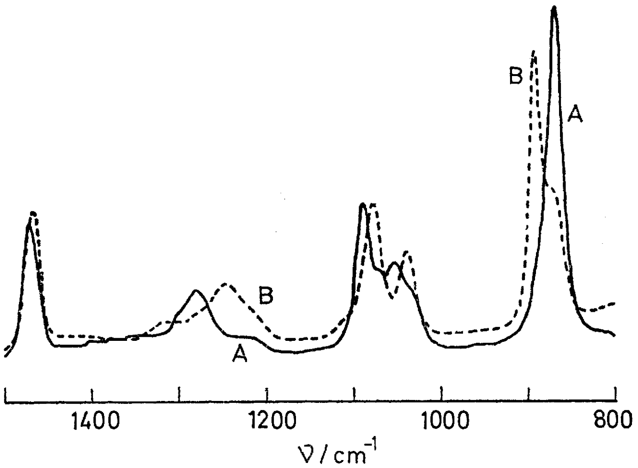

FIGURE 2 Raman spectra of the region 800—1 500 cm^{-1} for two glycol solutions: A, 5.0 mol % glycol, 95.0 mol % water; B, 5.0 mol % glycol, 85.0 mol % water, 10.0 mol % $CaCl_2$

Since, with the exception of zinc chloride, the salts are highly dissociated in water, the interactions taking place with EG are assumed to involve primarily the cations. To test this assumption the Raman spectra of EG solutions containing 5 mol % calcium chloride, bromide, or iodide were recorded. No differences were detected in the spectra.

In order to develop a more complete picture of the interactions with calcium, the EG spectrum was examined at several different concentrations of calcium chloride, with the EG concentration held constant at 5 mol %. Solutions containing calcium chloride at the following levels were studied: 2.5, 5.0, and 10.0 mol %. The bands observed in the resulting spectra are listed in Table 2. The changes produced in the spectrum of EG are clearly dependent on calcium ion concentration, and are more significant in some regions than in others. In the 1 200—1 350 cm^{-1} region, increasing the calcium chloride concentration results in a decrease in the intensity of the band at 1 274 cm^{-1} and a parallel increase in the intensity of a new band at 1 241 cm^{-1}. In addition, as the calcium chloride concentration is increased the four bands in the 1 000—1 100 cm^{-1} region appear to coalesce into two bands at frequencies lower than those of the two which are dominant in the spectrum of aqueous EG; in the presence of 10 mol % calcium chloride the amount of the shift is *ca.* 12 cm^{-1}. These effects are reflected in Table 2 and illustrated in Figure 2.

The most pronounced change associated with $CaCl_2$ addition occurs in the 800—900 cm^{-1} region. For the 2.5 mol % solution this region is similar to that in the EG–water spectrum; a strong band appears at 866 cm^{-1} with a shoulder at 885 cm^{-1}, somewhat more pronounced. As shown in Figure 3, the shoulder becomes a separate peak at 5 mol % calcium chloride; the region now contains peaks at 887 and 870 cm^{-1}. As also shown in Figure 3, at 10 mol % calcium chloride the dominant one is the 887 cm^{-1} band, and the peak at 870 cm^{-1} is reduced to a shoulder. The effects described above for calcium chloride are approximately duplicated where zinc chloride is the salt added. Strontium produces similar changes also, but they are less pronounced at any particular level of addition.

In order to interpret the observed spectral effects it is necessary to consider the molecular vibrations responsible for the bands in the regions most influenced by the presence of metal ions. Knetsch and Groeneveld [14] have recently reviewed the various assignments in the 800—1 100 cm^{-1} region. Because of their relevance to the present study the assignments will be reviewed briefly.

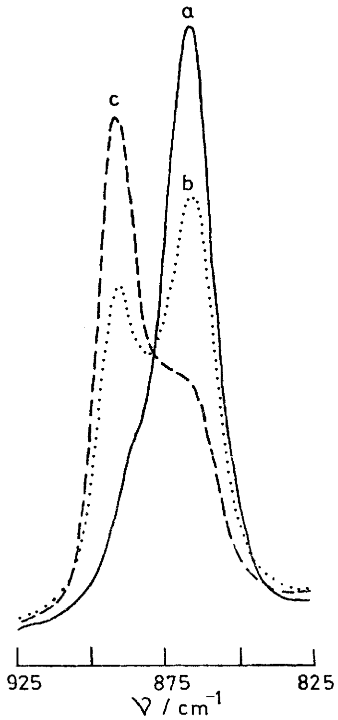

FIGURE 3 Changes in the C–C stretching band of aqueous ethylene glycol as the content of calcium chloride is changed; a, 5 mol % glycol, 95 mol % H_2O; b, 5 mol % $CaCl_2$, 5 mol % glycol, 90 mol % H_2O; c, 10 mol % $CaCl_2$, 5 mol % glycol, 85 mol % H_2O

Of particular importance are the bands in the 800—900 cm^{-1} region where the Raman spectrum of EG, both pure and in aqueous solution, contains one strong, highly polarized band at 865 cm^{-1} and a weak shoulder at *ca.* 885

cm^{-1}. The i.r. spectrum of EG contains, in the same region, two strong bands at 883 and 862 cm^{-1}, the former being slightly the more intense. A comprehensive study by Matsuura and Miyazawa[18] based on normal co-ordinate analyses of several geometries of the EG molecule found the 862 cm^{-1} band to be composed, predominantly, of the skeletal C–C stretching vibration, together with a C–O stretching component. They found the 883 cm^{-1} band to be due to a CH_2 rocking vibration also coupled with the C–O stretching motion. This interpretation is consistent with an analysis carried out in the present study, utilizing the force constants developed by Pitzner,[20] which resulted in the same interpretation of the two bands in the 800—900 cm^{-1} region. The attribution of the 862 cm^{-1} band primarily to the C–C stretching vibration which is symmetric under the point groups of most of the possible conformations, is supported by the high degree of polarization of the band in the Raman spectrum.

The bands between 1 000 and 1 100 cm^{-1} are even more difficult to interpret because of extensive vibrational coupling in this region. However, it is generally accepted that the C–O stretching modes contribute significantly to bands in this region. This also was indicated by the computations performed in the present study as well as by the calculations of Matsuura and Miyazawa.[18]

As noted above, all the Group II cations studied affected the bands in the 1 000—1 100 cm^{-1} region to some degree, while only calcium and zinc, and, to a lesser extent strontium, altered also the bands in the 800—900 cm^{-1} region. The difference in the nature and relative magnitude of the changes suggest that the two groups of ions are involved in different types of interactions with the EG molecules.

The two types of interactions most readily envisaged correspond, respectively, to mono- and bi-dentate co-ordination of the EG with the cations. Although this suggestion represents a departure from the interpretation put forth by Knetsch and Groeneveld[14,15] concerning co-ordination of glycol with Group II cations in the solid state, it appears to be a logical preliminary interpretation, the validity of which can be subjected to further experimental exploration. In terms of this interpretation, the minor changes in the spectrum of EG resulting from the presence of magnesium, barium, or cadmium ions are manifestations of monodentate co-ordination of the metal ions by the glycolic hydroxy-groups. The major changes in the spectrum arising from the presence of calcium, zinc, or strontium are, in contrast, attributed to bidentate co-ordination of the metal ions accompanied by significant conversion of glycol molecules from one conformation to another.

To provide a basis for comparison and to test the validity of the above interpretation the effects of calcium chloride on the Raman spectra of aqueous solutions of a number of related systems were explored. Methanol and ethanol were taken as representative of molecules for which monodentate co-ordination of the hydroxy-group is the only possible mode of interaction. The *cis*- and *trans*-cyclohexane-1,2-diols were chosen as molecules admitting bidentate co-ordination of the hydroxy-groups but without any attendant conformational changes. Finally, EDA was selected as a molecule for which both bidentate co-ordination and conformational changes are possible.

Although the effects of calcium chloride and of hydration on the Raman spectra of methanol have been reported[21,22] the published works did not adequately parallel conditions used in the present study for EG. Measurements were therefore made of the spectra of 5 mol % solutions of methanol and ethanol with varying amounts of calcium chloride. In the spectra of both methanol and ethanol solutions the C–O bands were shifted slightly to lower frequencies (*ca.* 10 cm^{-1}), broadened, and reduced in intensity; in the spectra of ethanol solutions the C–C band at 884 cm^{-1} and the methyl rocking band at 1 049 cm^{-1} were unaltered as the concentration of calcium chloride was increased.

The relatively minor changes observed in the spectra of methanol and ethanol are of the same order of magnitude as those induced in the spectrum of EG by magnesium, barium, and cadmium ions. Since only monodentate co-ordination is possible with methanol and ethanol, it appears reasonable to conclude that in the case of EG also co-ordination of these particular ions is monodentate.

The cyclohexane-1,2-diols should have the same capacity to form bidentate complexes as postulated for EG, but without the possibility of conformational change. In both *cis*- and *trans*-cyclohexanediols the rings are in chair form and the hydroxy-groups are in *gauche*-positions relative to each other. Bidentate co-ordination of metal ions is not likely to result in any conformational changes. There are no reasons, however, why any unusual electronic effects, which might arise from bidentate co-ordination of EG, would not also arise in the case of the cyclohexanediols.

The Raman spectra of both *cis*- and *trans*-cyclohexanediols in aqueous solutions, with and without 5 mol % calcium chloride, were recorded. For *cis*-cyclohexanediol, the spectra with and without calcium chloride were essentially indistinguishable. For the *trans*-cyclohexanediol there were some minor changes in the relative intensities of bands in the 1 100—1 150 and 1 300—1 400 cm^{-1} regions. There were, however, no changes in the locations of any of the bands.

EDA is the other common 1,2-disubstituted ethane capable of bidentate co-ordination. Theoretical studies by Jhon *et al.*,[23] indicate that the *trans*-form is the conformation of least energy. Furthermore, many studies

---

[20] L. J. Pitzner, Doctor's Dissertation, The Institute of Paper Chemistry, Appleton, 1973.

[21] R. E. Hester, and R. A. Plane, *Spectrochim. Acta*, 1967, **23A**, 2289.

[22] Z. Kecki, *Spectrochim. Acta*, 1962, **18**, 1165.

[23] M. S. Jhon, U. Cho, L. B. Kier, and H. Eyring, *Proc. Nat. Acad. Sci. U.S.A.*, 1972, **69**, 121.

of EDA complexes have shown that the ligand molecules take the *gauche*-form.[24-27] The similarities between the geometries of EG and EDA suggest that if the major changes in the spectrum of EG upon bidentate co-ordination are indeed due to conformational changes, then similar changes should be detectable in the Raman spectrum of EDA upon bidentate co-ordination of metal ions. In a study of the Raman spectra of EDA complexes with zinc, cadmium, and mercury, Krishnan and Plane [28] reported shifts in the C–C band to higher frequencies upon complex formation. Here again additional studies were indicated to more closely approximate the conditions previously used in the measurements on EG.

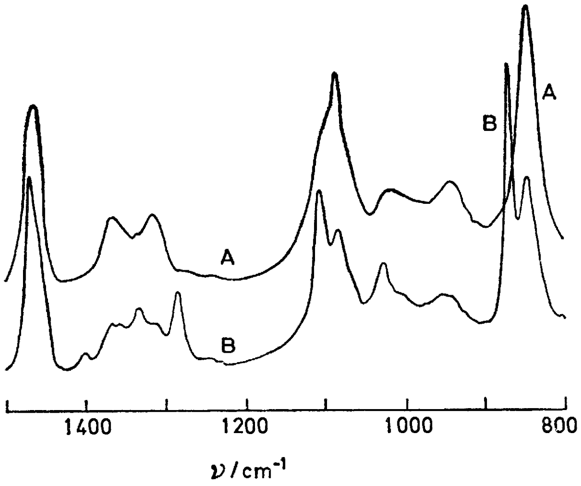

FIGURE 4 Raman spectra of the region 800—1 500 cm^{-1} for two ethylenediamine solutions: A, 5.0 mol % ethylenediamine, 95.0 mol % water; B, 5.0 mol % ethylenediamine, 90.0 mol % water, 5.0 mol % $CaCl_2$

Solutions containing 5 mol % EDA in water, with and without 5 mol % calcium chloride were prepared and their Raman spectra recorded. Though some of the EDA–calcium chloride complex precipitated at first enough remained in solution to give a suitable spectrum. The spectra in the 800—1 500 cm^{-1} region are compared in Figure 4. The differences are at least as dramatic as those in the spectra of EG with and without calcium chloride, and they are found in the same regions. Of particular interest is the change in the 800—900 cm^{-1} region which parallels almost exactly the pattern of change in the spectrum of EG. It thus appears that the changes observed in the spectrum of EG are indeed of the type that might be anticipated if a substantial fraction of the molecules undergo a change in conformation.

The comparisons of the effects of calcium chloride addition on the Raman spectra of the cyclohexanediols and EDA with its effects on the spectrum of EG provide support for the hypothesis that the spectral changes are due primarily to conformation changes. The question arises, however, of parallel effects on the i.r. spectrum. Though an investigation of the i.r. spectra of the aqueous solutions would have been desirable, it was considered beyond the scope of the present study. It was thought possible, however, to obtain some valuable information by examining the spectra of solutions of calcium chloride in pure EG. Differential spectra of such solutions against pure EG were recorded in the 800—1 150 cm^{-1} region, using the 862 cm^{-1} band to balance the absorption of the solvent. The difference spectra are compared with the i.r. spectrum of pure EG in Figure 5. It is clear that the difference spectra show increased absorption in the regions where new features appear or are intensified in the Raman spectra of the aqueous EG–calcium chloride solutions. The appearance of these bands is taken to confirm the interpretation set forth above for the features in the Raman spectra.

Conclusions.—The most significant result of the present study is the observation that calcium, zinc, and strontium ions can indeed enter into a complex with EG. Thus, bidentate co-ordination of these ions by isolated pairs of vicinal hydroxy-groups is possible, and the constraints suggested in the work of Angyal *et al.*[2,3] and of Richards [4] cannot be generalized beyond the conditions which they investigated. In this connection it should be noted that although Richards observed many complexes with zinc ions, Angyal [3] reports that the effect of zinc is barely noticeable.

The pattern of variation in the interactions between EG and the cations is not simply rationalized. Strong co-ordination by zinc is not surprising in view of its position in the Periodic Table, the stability of many of its complexes, and the results reported by Richards.[6] Equally strong co-ordination by calcium is not antici-

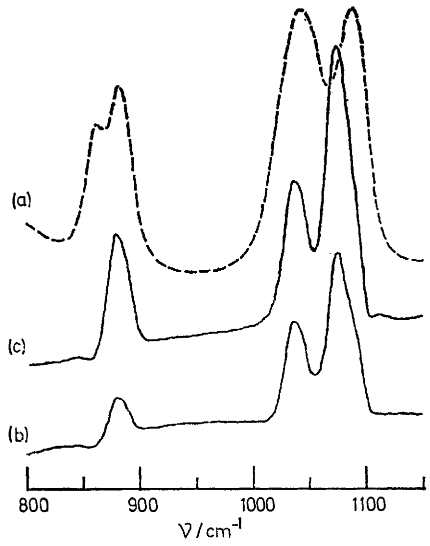

FIGURE 5 I.r. spectra: (a) ethylene glycol; (b) 5.0 mol % $CaCl_2$ in 95.0 mol % glycol *vs.* glycol reference; (c) $CaCl_2$ saturated glycol *vs.* glycol reference

---

[24] C. J. Hawkins, 'Absolute Configuration of Metal Complexes,' Wiley–Interscience, New York, 1971, p. 64.

[25] H. Scouloudi and C. H. Carlisle, *Nature*, 1950, **166**, 357.

[26] Reference 24, p. 278.

[27] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds.' Wiley–Interscience, New York, 1970, p. 224.

[28] K. Krishnan and R. A. Plane, *Inorg. Chem.*, 1966, **5**, 852.

pated *a priori*, however. Rationalizations in terms of electronegativity, charge : radius ratio, or accessible vacant orbitals would require for consistency that either cadmium or magnesium co-ordinate as strongly as calcium. Angyal's observation[3] that a radius of *ca.* 1.0 Å is the common characteristic of the co-ordinating metal ions does not fit the pattern reported above; the zinc ion has a radius of 0.74 Å while the radius of the cadmium ion is 0.97 Å.

More empirically, the indication of strong co-ordination of vicinal hydroxy-groups with calcium is consistent with the findings by Bugg and Cook[29] that bidentate co-ordination of calcium by carbohydrates is accompanied by significant distortions in the O–O distances and the skeletal angles of the vicinal hydroxy-groups involved in the co-ordination. Furthermore, the anomalous behaviour of magnesium within the patterns of co-ordination of Group II cations is not unknown;[3,30,31] steric hindrance of the ligand[32,33] and entropy effects,[34] both arising from the comparatively small size of the magnesium ion, have been cited as possible explanations of this behaviour.

Our results also have implications for the question of the dominant EG conformation in the liquid phase. Past studies have generally concluded that either the *gauche*-conformation alone is present, or that both conformations coexist, with the *gauche*-conformation dominant.[16–19,35–37] The present results, in contrast, suggest that the dominant form is the *trans*-conformation, since the conversion to the *gauche*-form upon bidentate co-ordination appears to be the only plausible explanation of the spectral changes observed.

We acknowledge experimental help from Mr. L. Sell and Mr. S. Nagel and Mr. S. Edwards and Mr. G. Watson for the normal co-ordinate analyses. Financial support of The Institute of Paper Chemistry is gratefully acknowledged.

[4/1909 *Received*, 18*th September*, 1974]

---

[29] C. E. Bugg and W. J. Cook, *Chem. Comm.*, 1972, 727.

[30] A. E. Martell and M. Calvin, ' Chemistry of the Metal Chelate Compounds,' Prentice Hall, Englewood Cliffs, 1959, p. 195.

[31] F. J. C. Rossotti, in ' Modern Coordination Chemistry,' eds. J. Lewis and R. G. Wilkins, Interscience, New York, 1960, p. 41.

[32] R. J. P. Williams, *J. Chem. Soc.*, 1952, 3770.

[33] R. A. Care and L. A. K. Staveley, *J. Chem. Soc.*, 1956, 4571.

[34] G. H. Nancollas, *J. Chem. Soc.*, 1956, 744.

[35] H. Matsuura, M. Hiraishi, and T. Miyazawa, *Spectrochim. Acta*, 1972, **28A**, 2299.

[36] K. G. R. Pachler and P. L. Wessels, *J. Mol. Struct.*, 1970, **6**, 471.

[37] Y. Kuroda and M. Kubo, *J. Polymer Sci.*, 1957, **26**, 323.