explanation for the metallic properties of NiV_2Se_4. Also, the smaller unit cell size noted earlier for NiV_2Se_4 is apparently primarily the result of metal–metal interactions affecting the *a* and *b* axial lengths.

Acknowledgment.—The authors wish to thank Dr. John B. Goodenough of the Lincoln Laboratory of Massachusetts Institute of Technology for his helpful comments.

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Vibrational Analysis of Some Oxyanion–Metal Complexes

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Received January 4, 1966

Normal coordinate calculations have been performed for metal complexes of the oxyanions nitrate, carbonate, sulfate, perchlorate, and phosphate. Force fields determined to give satisfactory frequencies for the uncomplexed oxyanions were perturbed in ways corresponding to metal binding and oxyanion polarization, and the effects on observable infrared and Raman vibrational frequencies were calculated. Comparisons are made between our calculated frequencies for the complexed oxyanions and experimental frequencies, enabling conclusions to be drawn about the relative importance of metal–oxygen bond formation and oxyanion polarization effects.

A considerable amount of experimental data has become available recently concerning the changes in infrared and Raman spectra of oxyanions such as carbonates, nitrates, phosphates, sulfates, and perchlorates upon metal complex formation. In order to extract from the reported frequency shifts and intensity changes some information about the physical nature of the interaction between metal ions and oxyanion ligands, we have undertaken a series of normal coordinate analyses of the molecular vibrations in complexes of these polyatomic ligand anions.

These calculations, the results of which we present here, were performed in the simplest permissible fashion, in order to show the trends of molecular deformation parameters, especially of the bond-stretching force constants, in a variety of forms and strengths of metal–ion association.

Normal Coordinate Calculations

The method of approach was identical for all molecules and consisted of first finding the simplest set of force constants which could give a set of frequencies for the normal modes of the free (uncomplexed) oxyanion in close agreement with observed frequencies.[2] A simple valence force field with one or two off-diagonal interaction force constants was found satisfactory in all cases. The calculations for the free oxyanions were all performed assuming symmetry point groups corresponding to the symmetries of the metal–oxyanion complexes investigated, but force constants for all modes involving metal motion were equated to zero. Thus, the factored secular determinants were divided into blocks corresponding to the irreducible representations of the point groups of the complexes, but these blocks contained identical eigenvalues owing to the artificial separation of degenerate modes. The oxyanion bond-stretching force constants were then changed so that the bond to the oxygen atom interacting with a metal ion was weakened, while the others were strengthened. This was done in such a way that the sum of the stretching force constants for all of the oxyanion bonds remained constant in all cases. This situation is believed to represent closely simple polarization of the oxyanions. Next the metal–oxygen bond force constant was increased from zero, leaving the oxyanion force constants at their values for the free anion. Finally, the metal–oxygen bond was given a finite force constant, and the polarization effect on the anion bonds to the oxygen atoms was redetermined.

Changes in off-diagonal elements of the force constant matrices, in bending force constants of the ligands, and in the Z–O–M bending force constants have been neglected. The directions and magnitudes of the first two effects are hardly predictable, even in a more elaborate force field approach, without a more detailed knowledge of charge distributions. For Z–O–M bending force constants also, it is virtually impossible to predict their behavior as M–O bond strength and ligand polarization increase. Certainly, it is likely that such effects will be small compared with the changes in stretching force constants considered in detail above. Incorporation of a Z–O–M bending force constant of 0.2 mdyne/A into the force field of C_{2v} nitrate complexes, for example, leaves all of the A levels unchanged and results mainly in an upward shift of the two B levels by only 10–15 cm^{-1}.

The standard Wilson *F–G* matrix method[3] of analyzing the normal modes of vibration was used throughout although several of the results could alternatively have been obtained by a simpler first-order perturba-

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[1] Chemistry Department, University of York, York, England.

[2] D. Koch and G. Vojta, *Z. Physik. Chem.*, **224**, 209 (1963).

[3] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

tion treatment of the proper ligand vibrations.[4] For the determination of the G matrices, use was made of the following simplifications. The bond distances and interbond angles in the trigonal and the tetrahedral oxyanions, respectively, were all taken as equal: 1.26 A and 120° for carbonate and nitrate, 1.51 A and 109.5° for phosphate, sulfate, and perchlorate.[5] These geometric data were assumed to be unchanged by coordination since the changes in bond-stretching force constants produced by coordination are expected to be of much greater significance. Metal–oxygen bond distances of 2.0 A were used throughout. For the masses of C and N an average value of 13 was used, as was 32 for the masses of P, S, and Cl. The mass of the metal ion was taken as 60 to cover the 3d metal ions from Mn to Zn. Even in cases where the mass of the metal would differ considerably from this value, no severe error is to be expected since the dynamic coupling of the M–O vibration to the ligand vibrations will be small compared to the "static" effect of the M–O force field experienced by the coordinated oxygen atom. Only if the M–O force constant is of comparable magnitude to the internal ligand force constants is dynamic coupling of importance.

Effects of complex formation on esters and anhydrides of phosphates of the general structure $ROPO_3$ were simulated by the structure $X–PO_3$, thus eliminating R–O stretching and R–O–P bending vibrations. For X an effective mass of 24 was assumed, which together with a P–X bond of 1.51 A gave a satisfactory fit of the free-ligand spectrum.

Results and Discussion

Nitrates and Carbonates.—The behavior of the vibrational levels of nitrates and carbonates under the influence of increasing M–O bond strength and increasing polarization is depicted in Figure 1 for the case of coordination along one of the C_2 axes[6] (over-all symmetry of complex assumed C_{2v}). The antisymmetric stretching frequencies are seen to be but little affected even by large M–O force constants (Figure 1b). The predicted small splitting of the degenerate E′ antisymmetric stretching modes could hardly be detected experimentally. Polarization of a ZO_3 oxyanion, however, induces a much larger splitting of the formerly degenerate antisymmetric stretching modes, as shown in Figure 1a. A difference, ΔF_{ZO}, in force constants for the bonds to the bound and free oxygen atoms of 1 mdyne/A would split the two levels by approximately 50 cm^{-1}.

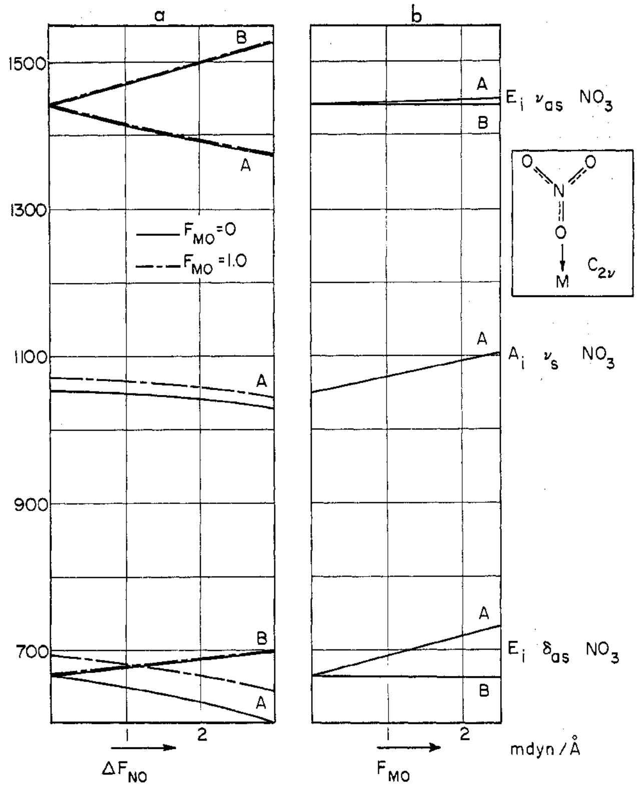

Figure 1.—Calculated fundamental frequencies in an NO_3^- (or a CO_3^{2-}) anion and frequency shifts by M–O bond formation and polarization in a complex with C_{2v} symmetry. The free-anion force constants (in mdynes/A) are F_{NO} = 6.35, F_{NO}' = 2.05, and $F\alpha_{(ONO)}$ = 0.54. The latter two constants remain unchanged throughout, while F_{NO} becomes F^f_{NO} and F^b_{NO} in the complex, representing the free and the bound N–O, respectively: (a) polarization effects; (b) metal-binding effects.

The symmetric stretching mode is seen to be slightly raised by increasing the M–O bond strength and lowered by the polarization effect. The net result of both effects operating together would be to produce but little change in this A level from its value in the free ligand.

The opposing effects of increasing M–O force constants and increasing polarization on the A and B components of the E′ modes are evidently a general feature of these C_{2v} complexes with a linear Z–O–M bond arrangement.[7] An interesting crossover of the A and B mode frequencies resulting from removal of degeneracy from the E′ deformation mode of the free ZO_3 anions is seen to occur by the opposing effects of polarization and M–O bond formation, resulting in an accidental degeneracy of the A and B modes. Such a coincidence probably is responsible for the absence of a separate B mode in the spectrum of the coordinated nitrate ion.[8-10]

The out-of-plane vibrations of nitrate and carbonate have not been considered in this treatment. It is

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[4] J. Mathews and R. L. Walker, "Mathematical Methods of Physics," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 10.

[5] Actual bond distances are 1.22 A in $NaNO_3$ and 1.29 A in $CaCO_3$ (R. L. Sass, R. Vidale, and J. Donohue, *Acta Cryst.*, **10**, 567 (1957)); 1.51 A in $Na_4P_2O_{10}\cdot 10H_2O$ (D. W. J. Cruickshank, *ibid.*, **17**, 672 (1964)); 1.52 A in K_2SO_4 (M. T. Robinson, *J. Phys. Chem.*, **62**, 925 (1958)); and 1.43 A in NH_4ClO_4 (H. G. Smith and H. A. Levy, *Acta Cryst.*, **15**, 1201 (1962)).

[6] Complete details on the force constant programs used in all of these calculations have been set out in tabular form and deposited as Document No. 8820 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

[7] Within a linear Z–O–M arrangement, the M–O force constant experienced by the bound oxygen atom is equivalent to an increase of the stretching force constant of the Z–O bond involved in metal binding. Thus, it opposes the polarization effect, which tends to decrease this force constant.

[8] R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 769 (1964).

[9] R. E. Hester and R. A. Plane, *J. Chem. Phys.*, **40**, 411 (1964).

[10] R. E. Hester, R. A. Plane, and G. E. Walrafen, *ibid.*, **38**, 249 (1963).

clear that this type of mode will not be affected by metal binding or by oxyanion polarization since the displacement vector of the bound oxygen atom is perpendicular to the M–O bond, and there is no coupling with inplane vibrational modes. Consequently, a change in the experimentally observed frequency of this out-of-plane mode probably would be indicative of a nonplanar configuration.

Further calculations of the splitting pattern produced by metal coordination with trigonal-planar ZO_3-type ions were performed using a model with the Z–O–M bonds nonlinear. With the M atom in the plane of the ZO_3 unit, the over-all symmetry was then lowered to C_s. An M–O–Z angle of 120° was assumed. The force constant variations and resulting frequencies are plotted in Figure 2. It is seen that the only significant difference in the splitting pattern from that of the C_{2v} complex is that the effect of formation of an M–O bond on the in-plane deformation modes is here in the same direction as that of polarization. The net result of the two effects is now a splitting of the two levels by *ca.* 50 cm^{-1} under the same conditions as produced an accidental degeneracy in the C_{2v} case.

Vibrational spectra for monodentate carbonate complexes are available for cobalt(III) amino carbonate complexes. For these a normal coordinate analysis with a Urey–Bradley force field already has been carried out by Fujita, Martell, and Nakamoto.[11] A comparison of our results with theirs will be instructive. The observed splitting of the two antisymmetric stretching modes from a number of monodentate cobalt(III) carbonate complexes ranges from 80 to 107 cm^{-1}, which corresponds to a polarization separation between F^{b}_{CO} and F^{f}_{CO} of 1.5 to 2.0 mdynes/A. Here F^{f}_{CO} and F^{b}_{CO} indicate force constants between the carbon and the free and bound oxygen atoms, respectively. A ΔF_{CO} of this magnitude combined with an F_{MO} of 1 mdyne/A would leave the symmetric stretching frequency virtually unchanged. Experimentally, a small rise of 15–20 cm^{-1} is observed for this frequency, which could be explained by the presence of a somewhat stronger M–O bond. Fujita, Martell, and Nakamoto, in fact, assume a value of 2.0 for the force constant of this bond.[11]

Even more informative, with respect to the kind of coordination involved, is the behavior of the in-plane deformation modes. With the parameters derived as above, the linear C_{2v} model allows a splitting of no more than a few wavenumbers, while the nonlinear C_s model allows splitting by some 60–75 cm^{-1}. Experimentally, splittings of 60–90 cm^{-1} were found in the monodentate carbonate complexes investigated, suggesting strongly that coordination involves nonlinear M–O–C bonds. Fujita, Martell, and Nakamoto, from comparison of calculated and observed Co–O stretching frequencies, have arrived at the same conclusion.

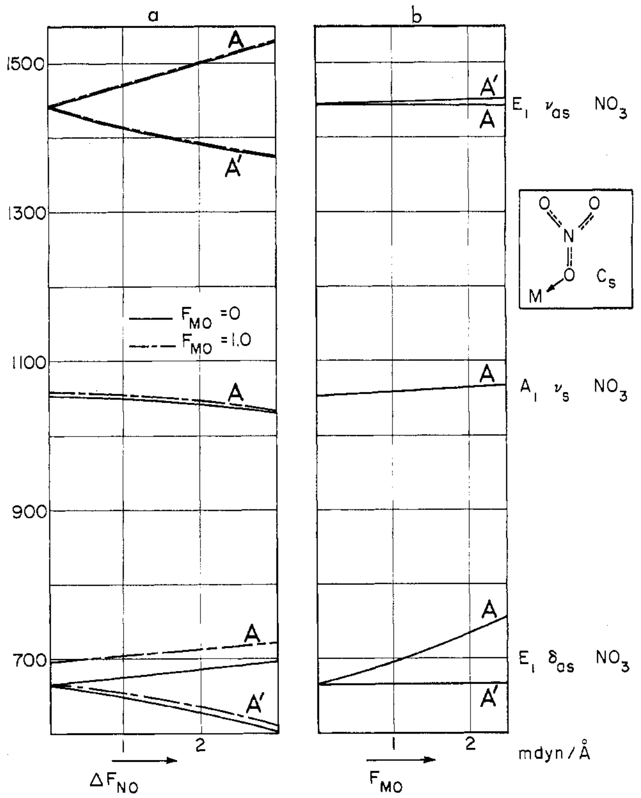

Figure 2.—Calculated fundamental frequencies in an NO_3^- (or a CO_3^{2-}) anion and frequency shifts by M–O bond formation and polarization in a complex with C_s symmetry. Force constant program identical with that of Figure 1: (a) polarization effects; (b) metal-binding effects.

Several experimental studies of nitrate complexes, on the other hand, have provided evidence that here at least in aqueous solution a linear arrangement with symmetry C_{2v} is present.[9,12,13] As mentioned earlier, there is experimental evidence which strongly suggests that an accidental degeneracy of the type predicted by our calculations for a C_{2v} complex occurs here. This is in the form of a widely varying degree of depolarization observed for lines characteristic of the bound nitrate ion, occurring in the in-plane deformation region, and the absence of a separate B_1 line in this region.[8-10] Our calculations indicate that exact coincidence of the E′ line of free nitrate with one of its components resulting from removal of degeneracy is extremely unlikely, particularly for the wide range of complexes studied. On the other hand, the close coincidence of the frequencies of the symmetric stretching modes of free and bound nitrate which is observed experimentally is fully consistent with the predictions of our calculations.

Few observations of metal–oxygen stretching modes have been made, but those which are available indicate that these fall in the region 250–450 cm^{-1}.[10,14] That a polarization effect also is important for coordinated nitrate is clearly indicated by the fact that the B_1 component derived from removal of degeneracy from the E′-type antisymmetric stretching modes of nitrate is consistently found to occur at higher

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(11) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).

(12) J. P. Mathieu and M. Lounsbury, *Discussions Faraday Soc.*, **9**, 196 (1950).

(13) J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

(14) J. R. Ferraro and A. Walker, *J. Chem. Phys.*, **42**, 1273 (1965).

frequencies than the A_1 component, as predicted by our calculations (see Figure 1). This assignment has been made unambiguously on the basis of degrees of depolarization of Raman lines, the A_1 line being polarized, the B_1 line depolarized.

In some solid nitrates, where the main perturbation of the nitrate ion is believed to be due to coordination of one of the oxygen atoms to the cation,[13] values for ΔF_{NO} on the order of 2.5 and >3 mdynes/A are derived for tervalent and quadrivalent cations, respectively, from the reported data.

Phosphates.—Linear coordination of a metal ion along one of the P–O bond directions has been considered in our calculations, leaving the complex with C_s symmetry. Any other arrangement of the M–O bond in the X–P–O plane will result in very similar changes of the vibration levels, with the exception of the PO_3 umbrella motion. This is completely unperturbed in the linear model, but would also suffer some perturbation in any other configuration. The perturbations of the phosphate normal vibrations resulting from coordination differ significantly from those of the ZO_3 molecules discussed in the previous section, as is seen in Figure 3.[6]

For phosphate complexes, frequency shifts with changes in force constants are nonlinear, unlike the nitrate and carbonate cases. The A′ component of the antisymmetric stretching mode is seen to decrease at first as ΔF_{PO} is increased, but at higher values of ΔF_{PO} the frequency rises again. This upward curvature is matched by a downward curvature of the frequency of the symmetric stretching mode. Evidently, the two A′ levels interact and repel each other increasingly as ΔF_{PO} is raised. Effects of the mutual admixture of these modes on intensities will be discussed below.

Our calculations are seen to predict a lesser splitting of the antisymmetric stretching modes for a given perturbation of phosphate than is the case for nitrate or carbonate. The contrast between phosphate and nitrate or carbonate is still more marked in the lower frequency deformation modes. Figure 3 shows these modes to be scarcely influenced by polarization and M–O bond formation.

Experimentally, infrared spectra of diphosphate and other phosphate esters complexed with Cu(II), Zn(II), and Be(II) show splitting of the antisymmetric stretching modes by *ca.* 60 cm^{-1}.[15] This corresponds to a degree of polarization of phosphate with ΔF_{PO} = 1.5–2.0 mdynes/A (see Figure 3a). For this range of ΔF_{PO} the shifts in all the other modes are predicted to be only very small. In fact, it is found experimentally that, apart from the splitting of the antisymmetric stretching mode, the infrared and Raman bands of diphosphate solutions upon complex formation are but slightly shifted.[15,16] It is clear (from Figure 3b) that, if strong M–O bonding with but little polarization were responsible for the 60-cm^{-1} splitting, similar splittings of the low-frequency lines should also be observed. If polarization and M–O bonding are both operative, it is seen (Figure 3a) that the former effect greatly outweighs the latter.

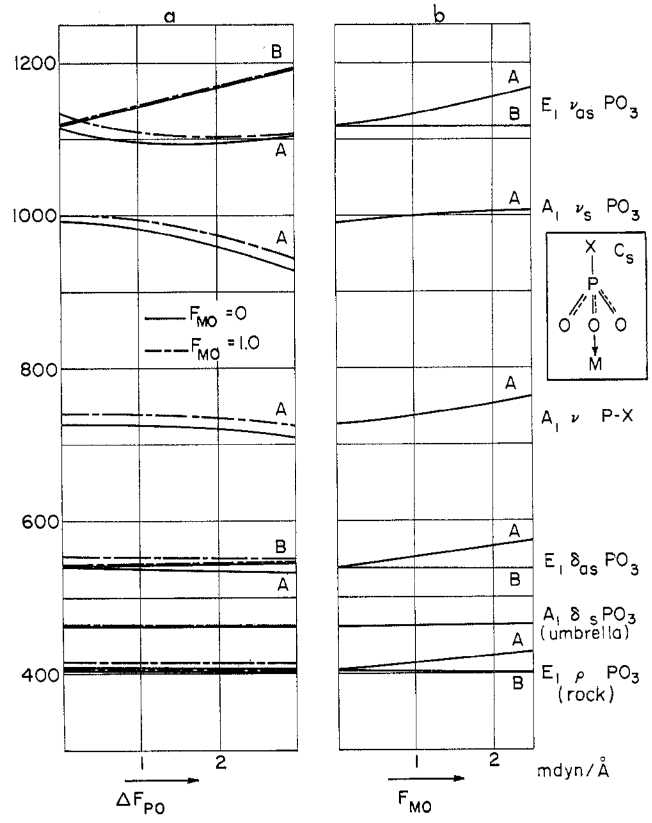

Figure 3.—Calculated fundamental frequencies in an $X-PO_3^{2-}$ anion and frequency shifts by M–O bond formation and polarization in a complex with C_s symmetry. The free-anion force constants (in mdynes/A) are F_{PO} = 6.35, F_{PX} = 4.50, $F\alpha_{(XPO)}$ = 1.30, and $F\alpha_{(OPO)}$ = 2.00. The latter three remain unchanged in the complex: (a) polarization effects; (b) metal-binding effects.

On complexation with other bivalent metal ions, such as Ni(II), Co(II), or Mg(II), phosphate ligands show a slight broadening of the antisymmetric stretching mode only.[15] Here, obviously, the splitting of its two components cannot be greater than *ca.* 20 cm^{-1}, which would result from ΔF_{PO} = 0.5–0.8 mdyne/A. In a variety of mixed complexes containing besides the diphosphate ligand, *e.g.*, oxalate, malonate, ethylenediamine, or dipyridine, the effectiveness of bivalent metal ions, such as copper or nickel, to induce splitting of the antisymmetric stretching mode is roughly the same as in the corresponding 2:1 complexes with diphosphate alone.

Sulfates and Perchlorates.—Formation of monodentate complexes with metal ions lowers the tetrahedral ZO_4 symmetry at least to C_{3v}. Our calculations were based on a model with a linear Z–O–M arrangement, giving the over-all ZO_4M complex C_{3v} symmetry. The splitting patterns and frequency shifts resulting from M–O bond formation and ligand polarization are represented in Figure 4.[6] These are seen to be qualitatively similar to those already discussed for phosphate, in that A_1 stretching modes vary nonlinearly with ΔF_{ZO}

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(15) H. Brintzinger, *Helv. Chim. Acta*, **48**, 47 (1965).
(16) H. Brintzinger and R. A. Plane, to be published.

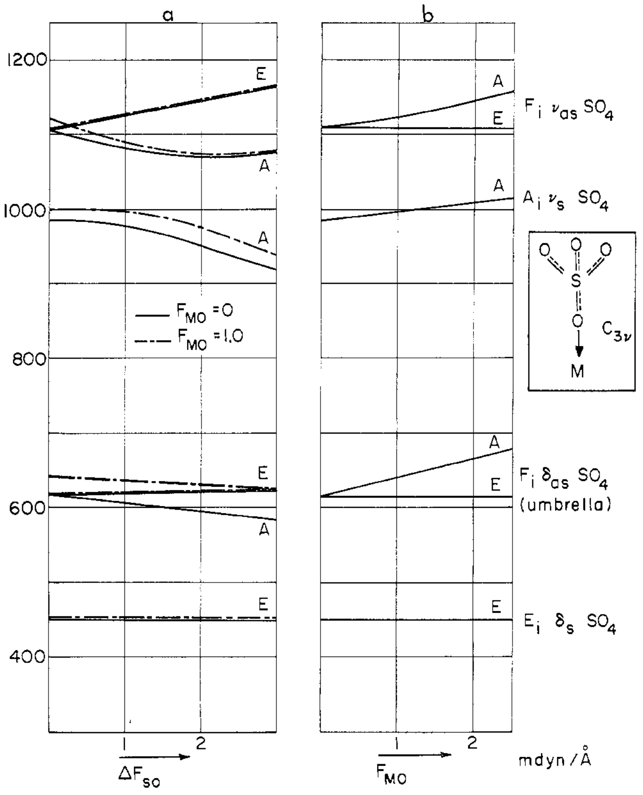

Figure 4.—Calculated fundamental frequencies in an SO_4^{2-} (or a ClO_4^-) anion and frequency shifts by M–O bond formation and polarization in a complex with C_{3v} symmetry. The free-anion force constants (in mdynes/A) are $F_{SO} = 6.60$, $F_{SO}' = 0.85$, $F_\alpha = 1.20$, and $F_\alpha' = 0.28$. The latter three remain unchanged in the complex: (a) polarization effects; (b) metal-binding effects.

(the polarization effect), and the splitting of the antisymmetric stretching modes is the most pronounced effect of coordination. Hester, Plane, and Walrafen's experimental results on the indium(III)–sulfate system[10] show good agreement with the predictions of our calculations and suggest that combination of M–O bonding and ligand polarization is responsible for the spectra obtained. The Raman line polarization data for the indium(III)–sulfate system establish unambiguously that the splitting of the two ligand F_2 modes results in the A_1 components being at higher frequencies than the E components in each case. This is opposite to the corresponding E′ mode splitting observed for nitrates and suggests that the ligand polarization effect is relatively less important here, M–O bond formation being the major factor determining the appearance of the complex spectra.

The M–O stretching frequency observed for the In–OSO_3 complex is 255 cm^{-1}, corresponding to a M–O force constant as high as 1.8 mdynes/A. Changes in the antisymmetric stretching region of the spectrum appear to be the most pronounced spectral effects of coordination, as predicted by our calculation.

For solid pentaamminecobalt(III) sulfate a splitting of the A_1 and E stretching modes by *ca.* 90 cm^{-1} has been reported,[17] corresponding to $\Delta F_{SO} > 2.0$ mdynes/A. In $[Cr^{III}(H_2O)_5SO_4]^+$ ν_{as} is split by 50 cm^{-1},[18] and in $CuSO_4 \cdot 5H_2O$ a splitting of *ca.* 60 cm^{-1} is found;[19] but, besides the coordination of the metal ion, other factors must be operative here to reduce the symmetry of the sulfate ion to a considerable extent since, even for the symmetric stretching vibration, ν_1, two bands are observed in the infrared spectrum of $CuSO_4 \cdot 5H_2O$. Variable degrees of broadening of the antisymmetric stretching band of some sulfates in aqueous solution have been correlated with differing degrees of inner- and outer-sphere complex formation.[19]

No conclusive spectral evidence for complex formation between perchlorate and metal ions in aqueous solutions has been found yet. In crystalline solids, however, some structure determinations have been reported recently where ClO_4^- is shown to be in monodentate coordination with bivalent metal ions.[20–23] The splittings observed here, if interpreted as mainly due to polarization by the monodentate coordination, would again correspond to $\Delta F_{ClO} \geqslant 2$ mdynes/A.

Intensities.—One of the main changes observed in infrared spectra of complexes of the oxyanions is the increased intensity of the symmetric stretching vibration. This feature can be explained by consideration of the way in which the eigenvector of this mode is perturbed by complex formation. As mentioned earlier, the A_1 component of the antisymmetric and the symmetric stretching modes suffer increasing mutual admixture as the polarization of the anion increases. In the nitrate and carbonate complexes this admixture is rather slight: even for the highest values of ΔF_{CO} considered, only *ca.* 10% of each of the modes is found to be mixed into the other. In complexes of the tetrahedral anions, on the other hand, this admixture is more extensive. With $\Delta F_{ZO} = 1.7$ the formerly symmetric ligand vibration is found to contain *ca.* 30% of the A_1 component of the antisymmetric Z–O stretch; when $\Delta F_{ZO} = 2.5$, both modes contain approximately equal contributions from both the symmetric and antisymmetric ligand-stretching vibrations. Thereby the absorption intensity of the antisymmetric vibration will of course be carried over into the formerly symmetric A mode, according to the degree of admixture. This is borne out strikingly in infrared spectra of pentaamminecobalt(III) carbonate and sulfate complexes, respectively, as reported by Nakamoto, *et al.*[17] In the CO_3 complex, the intensity of the symmetric vibration is only very small (*ca.* 10% of the intensity of the lower antisymmetric band) whereas in the sulfate this vibration acquires an intensity nearly equal to that of the low antisymmetric band.

In complexes of the diphosphate ion a similar behavior is observed as with sulfate: the symmetric stretching absorption which has very low intensity in the free ligand ion assumes an intensity of about half

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[17] K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4905 (1957).

[18] J. E. Finholt, R. W. Anderson, J. A. Fyfe, and K. G. Caulton, *Inorg. Chem.*, **4**, 43 (1965).

[19] R. Larsson, *Acta Chem. Scand.*, **18**, 1923 (1964).

[20] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965).

[21] A. E. Wickenden and R. A. Krause, *ibid.*, **4**, 404 (1965).

[22] F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, **87**, 4189 (1965).

[23] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

that of the lower antisymmetric band in the diphosphate complexes of Cu(II), Zn(II), and Be(II),[15] as would be predicted for $\Delta F_{PO} = 1.7$ present in these complexes. Simultaneously, with the increase of infrared intensity, the Raman intensity of the symmetric stretching vibration is decreased and is transferred to the antisymmetric stretching mode, so that the latter, which is Raman inactive in the free ligand, acquires appreciable intensity in diphosphate complexes.[16] In diphosphate complexes of, *e.g.*, Ni(II), Co(II), and Mg(II) the gain in infrared intensity of the symmetric stretching absorption is much smaller, corresponding to the smaller degree of polarization as judged by the minor splitting of the antisymmetric band.

The mutual admixture of symmetric and antisymmetric stretching vibrations is equivalent to a more or less complete decoupling of the stretching vibrations of the coordinated and of the free Z–O groups as the corresponding force constants $F^{b}{}_{ZO}$ and $F^{f}{}_{ZO}$ become different. This offers an explanation for the different behavior of carbonate and nitrate, on the one hand, and the phosphate, sulfate, and perchlorate anions, on the other. The heavier central atoms P, S, and Cl in the latter allow such a decoupling to occur more easily than do the light central atoms C and N.

Chemical Bonding in Oxyanion Complexes.—From the force constant data presented above, some information concerning the electron rearrangements associated with complex formation can be derived.

Bond orders in the coordinated Z–O groups are lowered considerably. If the rather well-documented view is accepted, that to a good approximation bond orders and stretching force constants in structurally related molecules exhibit a linear correlation,[24] numerical estimates for these bond orders may be made.

The reduction of the S–O stretching force constant from 6.6 mdynes/A in the free sulfate anion to 5.2 mdynes/A in pentaamminecobalt(III) sulfate would correspond to a reduction in bond order from 1.37[25] to 1.08. Similarly, in diphosphates the value of $\Delta F_{PO} = 1.7$ found for a number of bivalent metal complexes would correspond to a reduction of the PO bond order from 1.25[26] to 1.05 in the coordinated P–O group. Though these figures can, of course, not be regarded as very accurate, it seems obvious that most of the π_{dp} bonding between sulfur and oxygen or phosphorus and oxygen is abolished if the oxygen atom becomes involved in a sufficiently strong coordination. On a given oxyanion ligand, differing degrees of polarization are induced by different bivalent metal ions. The much lower ability of Co(II) and Ni(II) to polarize diphosphate, as compared with, *e.g.*, Zn(II), make it clear that the polarizing action of the metal is neither merely an effect of its electrostatic field nor a consequence of a π-acceptor action. Obviously, the degree of covalency of the coordinate bond must play a determining role in the reduction of bond order between the coordinated oxygen and the central atom Z.

Our hypothesis that the sum of the stretching force constants in an oxyanion stays virtually unchanged under the polarization perturbation induced by coordination of a metal ion is supported by the observation that the frequency of the symmetric stretching vibration is very little changed in the complexes of the oxyanions investigated. If anything, a very minor increase of the sum of the stretching force constants could be derived from comparison of experimental data with the results of our calculations. These findings would indicate that for any charge density that is withdrawn from a Z–O bond by coordination of the oxygen atom, an equivalent charge density flows in toward the central atom from the other uncoordinated oxygen atoms. Therefore, despite its considerable polarization, the oxyanion is left with the same sum of bond orders and hence also with the same effective charge on the central atom as in the uncomplexed state. This would lead directly to the conclusion that coordination of a metal ion cannot be an effective means of increasing the lability of the oxyanions toward a nucleophilic substitution. This view is borne out by the fact that only very slight enhancements of hydrolysis are brought about by coordination of bivalent metals to the PO_3 group of a phosphate ester or anhydride[27] and that carbonate does not acquire any appreciable lability toward substitution by hydroxide in the cobalt carbonates;[28] this is in contrast to quite dramatic enhancements of the hydrolysis of carboxylic esters[29] and of the decarboxylation of β-keto acids,[30] where no other double bonds are present to buffer away the increased electrophilicity resulting from the polarization of a C–O group by a metal ion.

Acknowledgments.—We wish to thank Professor R. A. Plane and Dr. J. A. D. Matthew for their interest in this work which was supported in part by NSF Grant No. GP2646 and a grant from the Office of Saline Water, U. S. Department of the Interior.

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[24] E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).

[25] T. V. Long and R. A. Plane, *J. Chem. Phys.*, **43**, 457 (1965).

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[27] R. W. Schneider and H. Brintzinger, *Helv. Chim. Acta*, **47**, 1717 (1964).

[28] H. Scheidegger and G. Schwarzenbach, *Chimia* (Aarau), **19**, 166 (1965).

[29] J. R. Cox and O. B. Ramsay, *Chem. Rev.*, **64**, 317 (1964).

[30] L. Meriwether and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 5119 (1956).