cm.$^{-1}$ region, there is a general correlation between the frequency and the ionic radii for all of the metal ions; as the ionic radius increases, the frequency decreases. Apparently the formation of the chelate ring and its resultant geometry has a direct effect on the C–N bond; the smaller ions cause the frequency to be higher. However, reference to Table I and the data for the tetrasodium salt of EDTA indicates that sodium ion does not follow the correlation observed for the other metal ions. Although its ionic radius is greater than that for Cd(II), the frequency for the corresponding peak is some 10 cm.$^{-1}$ higher. This inconsistent characteristic probably can be attributed to the absence of chelate rings in the sodium salt. The frequencies for the two peaks exhibited by the sodium salt should represent the C–N bond in the absence of chelate effects. The absence of significant differences in frequency between the tetrapotassium and tetrasodium salts confirms this supposition, especially in view of the marked difference in ionic radii for the two ions. For the metal chelates the shift to higher frequencies probably can be related to an increase in the strength of the N–metal bond. Smaller ionic radii would appear to favor formation of this bond and could account for the higher frequencies observed for Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Conclusion

The general trends of decreasing frequency with increasing ionic radii, which were observed for the alkaline earth chelates, are confirmed in the spectra for the eight metal chelates considered. The infrared data, especially for the carboxylate groups, support the conclusion that the bonding for the eight metal-chelates is primarily ionic. A carboxylate peak (C═O stretch) in the 1550–1610 cm.$^{-1}$ region is evidence for ionic bonding; other workers[12–14] have evidence for covalent bonding when this peak is at 1625–1650 cm.$^{-1}$. As noted previously,[2] a single sharp peak in this region supports the possibility of a coördination number of six for the divalent metal ions, but it does not prove its existence. The infrared method would be particularly effective in demonstrating that one or more of the carboxylate groups of EDTA is not bonded to the metal. Morris and Busch[12] have used this approach with particular effectiveness for the covalently bonded Co(III)–EDTA chelates. The presence of an extra peak in the 1600 cm.$^{-1}$ region is strong evidence for a coördination number other than six.

The data for Pb(II)–EDTA indicate that there is a difference between the four carboxylate groups (COO^-) in the chelate molecule. This could be accounted for if one or more of these groups were covalently bonded to the lead ion. However, the double peak for the CH_2 band (2900 cm.$^{-1}$, 2850 cm.$^{-1}$) would lend support to the alternate conclusion that one or more of the COO^- groups are unbonded to the lead ion. The latter conclusion would mean that Pb(II) has a coördination number of less than six in the EDTA chelate.

The similarity of all the infrared spectra in Fig. 1 and 2 would also support the conclusion that the bonding for these chelates is primarily ionic. Work in progress on higher valent metal ions indicates that the infrared spectra become more unique as the bonding increases in covalent character. The results of these investigations will be reported in the future.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CONNECTICUT]

Substitution in the Octahedrally Coördinated Cation Positions in Compounds of the Perovskite Type[1,2]

BY FRANCIS GALASSO, LEWIS KATZ AND ROLAND WARD

RECEIVED SEPTEMBER 18, 1958

Several phases with perovskite-type structures corresponding to the general formula $A^{II}(B_x^{II}B_y^{III}B_z^{V})O_3$ have been prepared where A^{II} = Ba, Sr; B^{II} = Sr, Ca, Zn, Fe, Co, Ni; B^{III} = Co, Fe; and B^{V} = Ta or Nb. A series of similar phases $A^{II}(Fe_{1-x}^{III}B_x^{V})O_{2.5+x}$ has also been made where x ranges from 0 to $^1/_2$. Other oxygen deficient phases include ordered compounds of the type $A^{II}(B_{1/2}^{II}B_{1/2}^{V})O_{2.75}$ where A^{II} and B^{II} are both alkaline earth ions. From X-ray powder patterns, the following phases appear to be of the cubic perovskite type with cell edges around 4 Å.: $Ba(Fe_{1/2}Ta_{1/2})O_3$; $Ba(Fe_{1/2}Nb_{1/2})O_3$; $Sr(Co_{1/7}^{II}Co_{2/7}^{III}Ta_{4/7})O_3$; $Ba(Zn_{1/3}Nb_{2/3})O_3$; $Ba(Zn_{1/5}Fe_{1/5}^{III}Nb_{3/5})O_3$; $Sr(Zn_{1/3}Ta_{2/3})O_3$; $Ba(Co_{1/3}Nb_{2/3})O_3$. $Ba(Ba_{1/2}Nb_{1/2})O_{2.75}$ and $Sr(Sr_{1/2}Nb_{1/2})O_{2.75}$ are typical of ordered, oxygen deficient phases which require a doubling of the 4 Å. unit cell edge but retain cubic cell shape. For some of the $Sr^{II}(B_{1/3}Ta_{2/3})O_3$ compounds, the powder patterns appear to require a tripling of the 4 Å. unit cell edge. A number of other perovskite-like phases were prepared which gave rather more complex powder patterns; these patterns could, however, be related to a small cubic pseudocell for comparison.

Introduction

The perovskite structure has been found to lend itself to wide departures in composition from the ideal formula ABO_3. Variation may be achieved by isomorphous substitution of either the A or B cations, by valence compensation and by cationic and anionic deficiencies. In many instances, composition changes are accompanied by structural variations, both of which may have profound effects upon the electrical and magnetic properties of the crystals.

Numerous phases typified by the formulas $(BaK)(TiNb)O_6$ and $Ba_3(NiTa_2)O_9$ having the

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(1) This research was sponsored by the Office of Naval Research. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) Part of this work was abstracted from the Master's Thesis of Francis Galasso, University of Connecticut, 1957.

perovskite structure have been prepared by Roy[3] who found that a combination of divalent ions in the A position with divalent and pentavalent cations in the B position was particularly favorable to the assumption of the perovskite lattice.

Steward and Rooksby[4] have shown that compounds of the type R_3WO_6, where R is an alkaline earth element, have a structure which can be regarded as an ordered perovskite type in which $^1/_3$ of the R cations as well as the W atoms, occupy positions of sixfold coördination. The compounds can therefore be represented by the formula $A(A_{0.5}W_{0.5})O_3$. The ordered arrangement of W and R cations is such as to lead to a face centered lattice.

The preparations described in this paper were undertaken to provide further examples of substitution in the B cation position using the valence compensation principle without involving the A cation.

Our attention was drawn to the remarkable stability of phases of the type $A^{II}(B^{II}_{1/3}B^{V}_{2/3})O_3$ from the results of an experiment designed to produce a ternary compound of tantalum(IV) by heating a mixture of strontium oxide, tantalum pentoxide and metallic zinc. The product was a mixture of a black and a white phase. The former was not identified, but the latter proved to be the compound $Sr(Zn_{1/3}Ta_{2/3})O_3$, which had the perovskite structure and could be synthesized readily in a fairly pure form by heating appropriate mixtures of the oxides.

Experimental

Reactants.—CaO, MgO and NiO were prepared by heating the corresponding reagent grade carbonates in air at 900 to 1000°. Cobalt carbonate gave Co_3O_4 under these conditions. CoO was obtained from the carbonate by heating in carbon dioxide. SrO was made by heating the carbonate at 1150° for 48 hr. in a stream of hydrogen and BaO by decomposing the peroxide at 950° *in vacuo*. The Fe_2O_3, Fe_3O_4, Fe, ZnO, Nb_2O_5 and Ta_2O_5 used were reagent grade chemicals.

Preparation of Samples.—A uniform procedure as previously described[5] was adopted for the preparation of samples. It consists essentially of heating at 1000° mixtures of oxides *in vacuo*. The stoichiometry was derived from the general formula $A^{II}(B_x{}^{II}B_y{}^{III}B_z{}^{V}/)O_3$ where A^{II} is strontium or barium, B^{II} = Sr, Zn, Fe, Mg, Co or Ni, B^{III} = Fe or Co, B^V = Nb or Ta. Compounds containing Fe^{II} were obtained by using equimolar proportions of Fe_2O_3 and Fe in the mixture of reactants. For the preparation of anion-deficient phases, the formula $A^{II}(B_{1-x}{}^{III}B_x{}^{V})O_{2.5+x}$ was used. Although all of the compounds were prepared *in vacuo*, many of those which had no oxidizable cations were also prepared in air.

Results

In all instances, but one, the products were microcrystalline powders. While a few of these gave X-ray diffraction patterns which could be completely indexed on the basis of a simple cubic ideal perovskite cell, most of the samples gave patterns which contained additional lines which might have been due to impurities, distortion from cubic symmetry and/or larger cell size. Some of these samples were given additional heat treatment or subjected to extraction with solvents to see if the patterns could be modified. Eventually, for the sake of comparison, they were indexed on the basis of the small cubic pseudo unit cell to which they were obviously related. Intermediate *d* values were taken where line-splitting was observed.

The dimensions of the cubic pseudocells for several phases of the type $A^{II}(B^{II}_{1/3}B^{V}_{2/3})O_3$ are listed in Table I. The precision of these measurements is not high since in many cases the back-reflection lines of the diffraction patterns were somewhat diffuse. The more precise values given are taken from the data of Roy.[3] It can be seen that the lattice constants vary in the expected manner with the change in ionic radius of the cations. This provides some justification for considering these phases to be of essentially the same type. The strontium–zinc compound was examined more closely than the others. Table II shows that the observed relative intensities of the X-ray reflections agree very well with those calculated for the cubic perovskite of composition $Sr(Zn_{1/3}Ta_{2/3})O_3$. The density of the powder was found to be 7.15 g./cc. giving the unit cell formula weight 276, compared with the theoretical 275. The chemical analysis of the corresponding compound contain-

TABLE I

LATTICE CONSTANTS FOR PEROVSKITE TYPE COMPOUNDS OF THE FORMULA $A^{II}(B_{1/3}{}^{II}B_{2/3}{}^{V})O_3$

	Compound	Pseudocell edge (Å.)	Radius[c] of B^{II} cation (Å.)
Sr	$Zn_{1/3}Ta_{2/3}O_3$	4.01[a]	0.83
	$Zn_{1/3}Nb_{2/3}$	4.00	.83
	$Co_{1/3}Ta_{2/3}$	4.00	.78
	$Mg_{1/3}Ta_{2/3}$	4.000[b]	.75
	$Ni_{1/3}Ta_{2/3}$	3.99	.74
Ba	$Sr_{1/3}Ta_{2/3}O_3$	4.25	1.18
	$Zn_{1/3}Ta_{2/3}$	4.10	0.83
	$Zn_{1/3}Nb_{2/3}$	4.10[a]	.83
	$Fe_{1/3}Ta_{2/3}$	4.10	.80
	$Co_{1/3}Ta_{2/3}$	4.086[b]	.78
	$Co_{1/3}Nb_{2/3}$	4.09[a]	.78
	$Mg_{1/3}Nb_{2/3}$	4.09	.75
	$Ni_{1/3}Ta_{2/3}$	4.075[b]	.74
	$Ni_{1/3}Nb_{2/3}$	4.065[b]	.74
	$Ni_{1/6}Zn_{1/6}Nb_{2/3}$	4.08	

[a] Cubic cell of edge indicated accounts for all observed lines. [b] Cell edge from paper by Roy.[3] [c] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948, Table III.

TABLE II

COMPARISON OF OBSERVED AND CALCULATED INTENSITIES OF REFLECTIONS FOR $Sr(Zn_{1/3}Ta_{2/3})O_3$

hkl	*I* (calcd.) × 10^3	*I* (obsd.)
100	227	M
110	8870	VVS
111	1	VVW
200	496	S
210	85	W
211	606	S
220	294	M
221	25	
300	6	VW
310	254	M
311	1	VVW
222	101	W

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[3] R. Roy, *J. Am. Ceram. Soc.*, **37**, 581 (1954).

[4] S. G. Steward and H. P. Rooksby, *Acta Cryst.*, **4**, 503 (1951).

[5] M. Kestigian, J. G. Dickinson and R. Ward, THIS JOURNAL, **79**, 5598 (1957).

ing barium instead of strontium gave Ba = 42.37%, Zn = 6.48%, Ta = 37.13%. The values calculated for Ba(Zn$_{1/3}$Ta$_{2/3}$)O$_3$ are Ba = 41.92, Zn = 6.64, Ta = 36.78.

A phase for which the starting composition was Ba(Ca$_{1/3}$Ta$_{2/3}$)O$_3$ was also prepared. The powder pattern of the product indicated that a quadrupling of the 4 Å. pseudocell edge might be necessary to index the extra lines. It is therefore open to doubt that a compound of the same composition as the starting mixture was obtained.

A number of perovskite-like phases containing trivalent ions in the B position were prepared. Examples of these are listed in Table III. It is possible to obtain a continuous series from BaFe$_{1/3}{}^{II}$Ta$_{2/3}$)O$_3$ through Ba(Fe$_{1/2}{}^{III}$Ta$_{1/2}$)O$_3$ to the oxygen deficient phase BaFeO$_{2.5}$. The only one in the series which appears to be cubic is Ba(Fe$_{1/2}{}^{III}$Ta$_{1/2}$)O$_3$. Analysis of this compound gave Ba, 44.21%; Ta, 29.43%; Fe, 9.31%. The theoretical values are 45.21, 29.76, 9.16%, respectively. The small cell size, *a* = 4.06 Å., admits only one Ba(Fe$_{1/2}$Ta$_{1/2}$)O$_3$ per unit cell so that the iron and tantalum must be randomly arranged. There is, of course, always the possibility that some very weak lines, which could indicate ordering, were overlooked. However, the intensities of "extra" lines which would result if the iron and tantalum were in the type of ordered arrangement already noted in the R$_3$WO$_6$ compounds depend on the difference in atomic scattering factors for iron and tantalum. This difference is large enough so that it is unlikely that such additional lines could have been overlooked if present. Attempts to prepare an ordered phase by annealing this compound at temperatures from 800 to 1000° were unsuccessful. It is interesting that ferroelectric properties have been observed for this compound (private communication from I. Lefkowitz). In preparing a sintered sample for ferroelectric measurements, the sample of Ba(Fe$_{1/2}$Ta$_{1/2}$)O$_3$ was heated in air at 1400°. An X-ray powder pattern of the sintered material was much sharper than that of the unsintered sample. All of the lines observed belong to the cubic perovskite type of pattern. No faint lines indicating ordering or distortion were seen. A photograph taken at 130° showed thermal expansion but no structural changes.

TABLE III

SOLID SOLUTIONS AND OXYGEN DEFICIENT PHASES

	Compound	Pseudocell edge
Ba	Fe$_{1/3}{}^{II}$Ta$_{2/3}$ O$_3$	4.10
	Fe$_{1/7}{}^{II}$Fe$_{2/7}{}^{III}$Ta$_{4/7}$	4.08
	Fe$_{1/2}{}^{III}$Ta$_{1/2}$	4.056[a]
	Fe$_{3/4}{}^{III}$Ta$_{1/4}$ O$_{2.75}$	4.07
	Fe^{III} O$_{2.5}$	4.08
Ba	Fe$_{1/2}{}^{III}$Nb$_{1/2}$ O$_3$	4.06[a]
	Fe$_{3/4}{}^{III}$Nb$_{1/4}$ O$_{2.75}$	4.07
	Fe^{III} O$_{2.5}$	4.08
Sr	Fe$_{1/2}{}^{III}$Nb$_{1/2}$ O$_3$	3.97
	Fe$_{7/10}{}^{III}$Nb$_{3/10}$ O$_{2.8}$	3.96[a]
	Fe^{III} O$_{2.5}$	3.96
Ba	Zn$_{1/5}$Fe$_{1/5}{}^{III}$Ta$_{3/5}$ O$_3$	4.08
	Zn$_{1/5}$Fe$_{1/5}{}^{III}$Nb$_{3/5}$	4.08[a]
	Co$_{1/7}{}^{II}$Co$_{2/7}{}^{III}$Ta$_{4/7}$	4.09
Sr	Co$_{1/7}{}^{II}$Co$_{2/7}{}^{III}$Ta$_{4/7}$	4.00[a]
	Zn$_{1/5}$Fe$_{1/5}{}^{III}$Ta$_{3/5}$	4.01[a]
Ba	Ba$_{1/2}$Ta$_{1/2}$ O$_{2.75}$	4.35[b]
	Ba$_{1/2}$Nb$_{1/2}$	4.34[b]
	Sr$_{1/2}$Nb$_{1/2}$	4.27[b]
Sr	Sr$_{1/2}$Ta$_{1/2}$	4.17[b]
	Sr$_{1/2}$Nb$_{1/2}$	4.17[b]
	Ca$_{1/2}$Nb$_{1/2}$	4.10[b]

[a] Cubic cell of edge indicated accounts for all observed lines. [b] Cubic cell of twice edge indicated accounts for all observed lines.

Products obtained from a mixture of barium oxide and tantalum pentoxide in which the ratio Ba/Ta was greater than three gave the pattern of a perovskite type of compound. A single crystal of this substance was obtained and precession photographs showed cubic symmetry. From the precession photographs a cell edge of 4.35 Å. was indicated, but weak reflections on a rotation photograph indicated that this cell edge should be doubled, *i.e.*, *a* = 8.70 Å. Analysis of the compound gave Ba/Ta = 2.98. The analysis and X-ray data are consistent with the formula Ba(Ba$_{1/2}$Ta$_{1/2}$)O$_{2.75}$. The powder photograph of the corresponding niobium containing compound was also examined and again several of the lines showed the necessity for a "doubled" cell with *a* = 8.68 Å. The measured density of Ba(Ba$_{1/2}$Nb$_{1/2}$)O$_{2.75}$ was 5.8 g./cc. corresponding to a formula weight of 288 (theoretical, 296). These phases, as well as some others listed in Table III, are similar to the barium tungsten oxides described by Steward and Rooksby[4] except that the compounds containing Nb and Ta are apparently oxygen deficient and have cells which are not distorted from cubic symmetry.[6] The unit cell of Ba$_3$WO$_6$ is reported to be considerably distorted from cubic symmetry. It would thus appear that the deficiency in oxygen in Ba$_3$NbO$_{5.5}$, for example, may be a contributing factor to the higher symmetry of its unit cell. There are other examples of higher symmetry going hand in hand with oxygen deficiency. The range of compounds SrV^{III}O$_{2.5}$ to Sr(V$_{1/2}{}^{III}$V$_{1/2}{}^{IV}$)O$_{2.75}$ appears cubic but attempts to prepare SrVO$_3$ led to heterogeneous products.[5] Again, BaTiO$_{2.5}$ is presumably cubic at room temperature whereas BaTiO$_3$ is tetragonal.

When a mixture of SrO and Ta$_2$O$_5$ corresponding to a Sr:Ta ratio of 2:1 was heated at 1250° for 24 hr., the product consisted of two compounds. One of these was a hexagonal phase, possibly Sr$_5$Ta$_4$O$_{15}$. The other was very similar to the cubic phase Sr(Sr$_{1/2}$Ta$_{1/2}$)O$_{2.75}$ except for a slightly shorter cell edge (8.30 Å. rather than 8.34 Å.) and some intensity changes. Two possibilities which suggest themselves are Sr$_{1-x}$(Sr$_{1/2}$Ta$_{1/2}$)O$_{2.75-x}$ and Sr(Sr$_{1/2-x}$Ta$_{1/2+x}$)O$_{2.75+1.5x}$, either of which could account for the type of intensity changes noted. By starting with a Sr:Ta ratio of 2.5 and heating at 1150° for 24 hr., the product obtained consisted almost entirely of the cubic phase (very little of the hexagonal phase was present).

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(6) While this manuscript was in preparation a publication by L. H. Brixner, THIS JOURNAL, **80**, 3214 (1958), appeared which described Ba$_3$TaO$_{5.5}$ and Sr$_3$TaO$_{5.5}$.

Discussion

With the exception of $\mathrm{Ba(Sr_{1/3}Ta_{2/3})O_3}$, the powder patterns of the compounds listed in Table I contained the lines of a cubic cell of the size indicated. These compounds may be considered as having undistorted pseudocells of cubic shape with an edge of about 4 Å. "Extra" lines were noted, however, in all cases except those designated by a superscript *a*. Almost all of the extra lines of the $\mathrm{Sr^{II}(B_{1/3}{}^{II}Ta_{2/3}{}^{V})O_3}$ compounds could be accounted for by a cubic cell of three times the indicated pseudocell edge.

For $\mathrm{Ba(Sr_{1/3}Ta_{2/3})O_3}$ that pseudocell was clearly distorted and the size reported was based on the first few lines of the photograph. The lattice may be rhombohedral with a unit cell edge about three times the indicated pseudocell edge and the rhombohedral angle close to 90°.

In Table III some series of solid solutions and some oxygen deficient phases are listed. Those compounds for which no "extra" lines were observed are designated by an *a*. Compounds which have cubic cells of twice the indicated pseudocell length, as previously discussed, are designated by *b*.

Some of the compounds listed in Table III may be considered solid solutions of other compounds listed in Tables I and III. For example, $\mathrm{Ba(Zn_{1/5}Fe_{1/5}{}^{III}Ta_{3/5})O_3}$ may be considered a solid solution of $\mathrm{Ba(Zn_{1/3}Ta_{2/3})O_3}$ and $\mathrm{Ba(Fe_{1/2}Ta_{1/2})O_3}$. Although it is possible that single phases exist over the complete ranges of solid solution, the only intermediate phases prepared in this study are those listed in the table.

Two factors which help determine whether an arrangement of different ions in B positions of a perovskite type structure will be ordered or random are ionic sizes and charge difference. The $\mathrm{A(B_{1/2}{}^{II}W_{1/2}{}^{VI})O_3}$ compounds, where A is Ba or Sr, have an ordered arrangement for a variety of B cations of different sizes.[4] Ordering can reduce local violations of Pauling's electrostatic valence rule and may therefore be expected in such an extreme case of ionic charge difference. Where the charge difference is not so great, as in the cases of $\mathrm{Ba(La_{1/2}Ta_{1/2})O_3}$,[6] which has an ordered arrangement of La and Ta, and $\mathrm{Ba(Fe_{1/2}{}^{III}Ta_{1/2})O_3}$, which, as prepared in this study, appears to have a random arrangement of Fe and Ta, size could be the determining factor. The size of the $\mathrm{La^{III}}$ ion (ionic radius = 1.15 Å.) would cause an ordered arrangement to be favored if the perovskite type structure is to be maintained, whereas the $\mathrm{Fe^{III}}$ ion (0.67 Å.) is small enough to be accommodated in a random arrangement. Such compounds as $\mathrm{Ba(Ba_{1/2}Nb_{1/2})O_{2.75}}$ and $\mathrm{Sr(Sr_{1/2}Nb_{1/2})O_{2.75}}$ have large ions in the B positions and the ordering observed is therefore to be expected. The ordering together with the oxygen deficiency may be the primary factors in the retention of cubic cell shape in these compounds.

STORRS, CONNECTICUT

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS AND THE LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

Molecular Complexes and Their Spectra. IX. Infrared Absorption by Iodine in its Pyridine Complexes and in Benzene

BY EARLE K. PLYLER AND ROBERT S. MULLIKEN

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When iodine and pyridine (Py) are dissolved together, the iodine fundamental vibration is absorbed rather strongly with a frequency ω_0 shifted from its vapor value (213 cm.$^{-1}$) to 184 cm.$^{-1}$ (in *n*-heptane) or 174 cm.$^{-1}$ (in benzene). In Bz (benzene), very much weaker absorption at 204 cm.$^{-1}$ is also observed. Quantitative intensity curves are shown. The shifted absorptions are ascribed, respectively, to a $\mathrm{Py{\cdot}I_2}$ or a $\mathrm{Bz{\cdot}I_2}$ charge-transfer complex (or perhaps contact, in the Bz case). Further details of interpretation and comparisons with other pyridine and benzene complexes of the halogens are given. Preliminary experiments showed that it is necessary to work with fairly fresh solutions, otherwise a band of unknown origin appears at 214 cm.$^{-1}$. Iodine in *n*-heptane (0.02 *M*) produces no new peaks near 200 cm.$^{-1}$.

Introduction

According to the quantum-mechanical theory of 1:1 donor–acceptor complexes with a halogen molecule X_2 or XY as acceptor, the X–X or X–Y bond should be loosened, the more so the greater the amount of negative charge transferred from the donor to the halogen molecule.[1] This loosening should be manifested by an increase in interatomic distance and a decrease in vibration frequency for the halogen. The former effect is best studied in solid compounds, and Hassel and collaborators have demonstrated its occurrence in a number of complexes with donors of the pyridine and the ether classes.[2] The latter effect is most easily studied by seeking the halogen molecule fundamental in the infrared absorption spectra of 1:1 complexes in solution.

Recently, D'Or, Collin and collaborators[3] have shown that (although the free halogen molecules Cl_2, Br_2 and I_2 are of course infrared-inactive) the infrared fundamental of Cl_2 and Br_2 appears, weakly and appreciably shifted toward lower frequency, in the absorption spectra of their solutions in benzene. This is what is expected if the halogen molecules are in part bound in charge-transfer complexes. However, for the halogens in benzene, perhaps the interactions should be described in terms of "contacts" rather than of complex-formation.[4] Still, it seems clear that they are in any

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[1] R. S. Mulliken, THIS JOURNAL, **74**, 811 (1952). II of the present series.

[2] O. Hassel, *Proc. Chem. Soc.*, 250 (1957); *J. Mol. Spec.*, 1958.

[3] J. Collin and L. D'Or, *J. Chem. Phys.*, **23**, 397 (1955); L. D'Or, R. Alewaeters and J. Collin, *Rec. trav. chim.*, **75**, 862 (1956).

[4] L. E. Orgel and R. S. Mulliken, THIS JOURNAL, **79**, 4839 (1957). VII of this series.