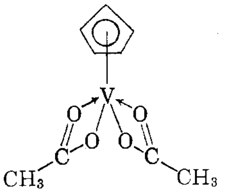

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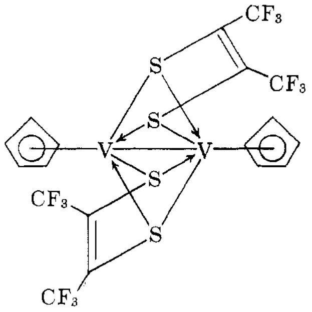

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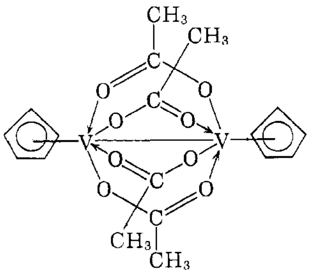

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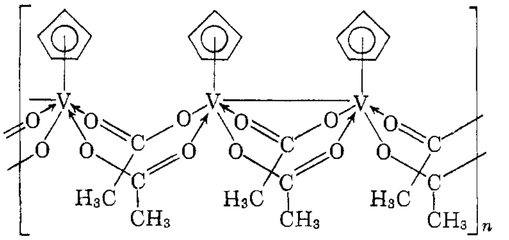

IV

Acknowledgment.—The author is indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grants AF-AFOSR-580-64 and AF-AFOSR-580-66, to Mr. M. B. Bisnette for experimental assistance, and finally to Mr. R. E. Rhodes and Mr. E. C. Horey for the mass spectral and magnetic susceptibility data.

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Raman Spectra of Tetrahalozincates and the Structure of Aqueous $ZnCl_4^{2-}$

BY CARL O. QUICKSALL AND THOMAS G. SPIRO

Received February 1, 1966

The stereochemistry of zinc(II) may involve either tetrahedral or octahedral coordination. Small donors such as fluorine and oxygen often exhibit a sixfold coordination as is found in the solids ZnF_2 (rutile structure)[1] and $(Zn(H_2O)_6)(ClO_4)_2$.[2] Larger donors prefer tetrahedral coordination. X-Ray diffraction studies have shown solid Cs_2ZnBr_4[3] and Cs_2ZnCl_4[4] to contain tetrahedral ZnX_4^{2-} species. Raman studies by Delwaulle[5] and others[6,7] have established a tetrahedral structure for ZnI_4^{2-} and $ZnBr_4^{2-}$ in aqueous solution. However, Irish, *et al.*,[8] argue from Raman evidence that $ZnCl_4^{2-}$ in aqueous solution is actually $ZnCl_4(H_2O)_2^{2-}$, with D_{4h} symmetry. If confirmed, this would represent an unusual and interesting difference between solution and crystalline structures of a complex ion.

We have recorded the Raman spectra of a series of cesium tetrahalozincates in order to investigate the vibrations of tetrahedral ZnX_4^{2-}. Comparison of solid and solution spectra strongly indicates that the conclusion of Irish, *et al.*, is unwarranted and that $ZnCl_4^{2-}$ is tetrahedral in solution.

Experimental Section

Cs_2ZnCl_4 and Cs_2ZnBr_4 were prepared by evaporation in dry air of aqueous solutions containing stoichiometric proportions of cesium halide and zinc halide. Cs_2ZnI_4 was prepared by evaporation in dry nitrogen of a 2.5 mole ratio mixture of CsI and ZnI_2 in water. In each case, small colorless crystals were obtained.

Raman spectra, at 28 ± 1°, were recorded with a Cary Model 81 Raman spectrophotometer using the 4358-A mercury line for excitation. The compounds were ground in a mortar and tapped into a conical sample holder, constructed after the design of Busey and Keller.[9]

Results and Discussion

The observed vibrational frequencies are presented in Table I with the results of others[5-8] on aqueous solution for comparison.

Four fundamental Raman-active internal vibrations are expected for a tetrahedral XY_4 molecule. Four bands are indeed observed for each compound and are assigned in the table. In no case was splitting of degenerate modes, from site symmetry or geometric distortion, observed. The four distinct bands found for Cs_2ZnI_4 justify our assumption that ZnI_4^{2-} is tetrahedral in this compound although its crystal structure has not been determined. The observed frequencies and assignments are quite reasonable in the light of the results of Delwaulle; Clark and Dunn[10] have observed ν_3 for Cs_2ZnCl_4 in the infrared at 292 cm^{-1}, in good agreement with our result.

The Raman spectra of ZnX_4^{2-} in aqueous solution show four distinct bands for ZnI_4^{2-} and $ZnBr_4^{2-}$ and two bands for $ZnCl_4^{2-}$: a polarized band in the stretching region at 280 cm^{-1} and a broad, depolarized band in the bending region at 80–120 cm^{-1}. Irish, *et al.*,[8] argue that the observation of only two bands, and particularly only one band in the bending region, indicates a nontetrahedral structure. They contend that the two bending modes observed for ZnI_4^{2-} and $ZnBr_4^{2-}$ should be more clearly resolved for $ZnCl_4^{2-}$.

The separation of ν_2 and ν_4 is somewhat larger in the cesium salts for $ZnCl_4^{2-}$ than for $ZnBr_4^{2-}$ or ZnI_4^{2-},

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[1] A. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 337.

[2] Reference 1, p 506.

[3] B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **12**, 744 (1959).

[4] B. Brehler, *Z. Krist.*, **109**, 68 (1957).

[5] M. L. Delwaulle, *Bull. Soc. Chim. France*, 1294 (1955).

[6] D. F. C. Morris, E. L. Short, and D. N. Waters, *J. Inorg. Nucl. Chem.*, **25**, 975 (1963).

[7] W. Yellin and R. A. Plane, *J. Am. Chem. Soc.*, **83**, 2448 (1961).

[8] D. E. Irish, B. McCarroll, and T. F. Young, *J. Chem. Phys.*, **39**, 3436 (1963).

[9] R. H. Busey and O. L. Keller, *ibid.*, **41**, 215 (1964).

[10] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).

TABLE I

RAMAN FREQUENCIES FOR ZnX_4^{2-} SPECIES (CM^{-1})[e]

Assignment	Cs_2ZnCl_4	$(ZnCl_4^{2-})$ (aq)	Cs_2ZnBr_4	$(ZnBr_4^{2-})$ (aq)	Cs_2ZnI_4	(ZnI_4^{2-}) (aq)
ν_1 (A_1)	288 s	280,[a] 278,[b] 275[c]	178 s	172,[a] 172,[c] 172[d]	130 s	122[a]
ν_2 (E)	116 w	82–116,[a] 110,[b] 79[c]	80 m	61,[a] 66,[c] 63[d]	60 w	44[a]
ν_3 (F_2)	298 m	280,[a] 278,[b] 306[c]	212 m	210,[a] 208,[c] 213[d]	172 w	170[a]
ν_4 (F_2)	130 w	82–116,[a] 110,[b] 104[c]	89 m	82,[a] 88,[c] 81[d]	70 w	62[a]

[a] Reference 5. [b] Reference 8. [c] Reference 6. [d] Reference 7. [e] Band description: s, strong; m, medium; w, weak.

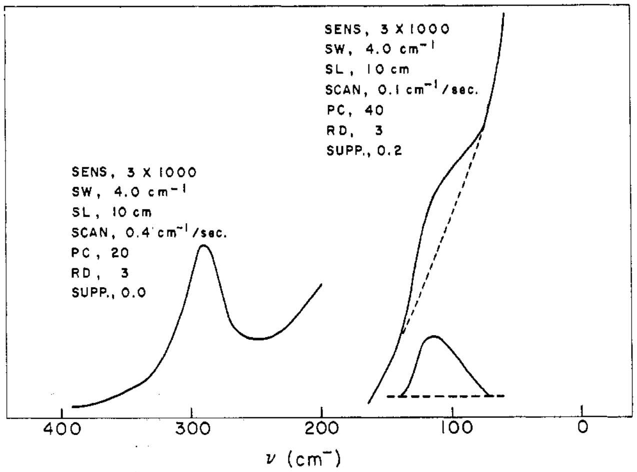

Figure 1.—Raman spectrum of 2.88 M $ZnCl_2$–9.35 M HCl aqueous solution showing a horizontal projection of 110-cm^{-1} band. A Cary Model 81 Raman spectrophotometer and a 15-amp lamp current were used. Abbreviations: SENS = sensitivity setting, SW = slit width, SL = slit length, SCAN = scan speed, PC = period control, RD = Raman dynode setting, and SUPP = zero suppression setting.

but the difference is only 5 cm^{-1}. The low-frequency solution band for $ZnCl_4^{2-}$ is quite broad in the published spectra.[5,8] Figure 1 shows this band as obtained in our laboratory for a solution containing 2.88 M $ZnCl_2$ and 9.35 M HCl. It is centered at 110 cm^{-1} and has a width at half-height of 40 cm^{-1}. We expect that if $ZnCl_4^{2-}$ remains tetrahedral on dissolution, the ν_2 and ν_4 frequencies should decrease by about the same amount (~16 and ~8 cm^{-1}, respectively) as for $ZnBr_4^{2-}$ and ZnI_4^{2-}. The resulting frequencies at 100 and 122 cm^{-1} could clearly both be contained in the observed solution band. It would appear that the two tetrahedral bending modes of $ZnCl_4^{2-}$ are simply broadened and merged into one envelope by interaction with the aqueous medium. A similar phenomenon has been observed for the tetrahalo complexes of thallium(III). Here also solution Raman spectra show two bands in the bending region for $TlBr_4^-$,[11] but only one for $TlCl_4^-$.[12]

Direct evidence that all three tetrahalo species remain tetrahedral upon dissolution is provided by the symmetric stretching frequency (ν_1), which is lowered by only 6–8 cm^{-1} in each case. Since ν_1 is primarily a measure of the Zn–X stretching force constant, and therefore presumably of the Zn–X bond strength, one would certainly expect a change in coordination of $ZnCl_4^{2-}$ to produce a much greater lowering of ν_1 due to weakening of the Zn–Cl bonds through increased Cl–Cl repulsion and the necessary rehybridization of the zinc orbitals. Any reasonable bonding scheme for square-planar $ZnCl_4^{2-}$ must involve the outer 5s, 5p, or 4d orbitals of zinc. Such a structure could be stabilized by the coordination of two waters at the *trans*-octahedral positions, but the Zn–Cl bonds themselves would be weaker than in tetrahedral $ZnCl_4^{2-}$. There is no known precedent for the proposed $ZnCl_4^{2-}$ (T_d) → $ZnCl_4(H_2O)_2^{2-}$ (D_{4h}) transformation. However, there are a number of transformations of the type MX_4^z (T_d) → MX_6^{z-2} (O_h), and every case for which spectral data are available involves a marked reduction in the symmetric stretching frequency; *e.g.*, for $SnCl_4$, ν_1 = 368 cm^{-1},[13] and for $SnCl_6^{2-}$, ν_1 = 311 cm^{-1}.[14] Part of this reduction may be due to the increase in charge, but some of it must surely arise from changes in bond type and nonbonded repulsion. It seems to us that the only reasonable interpretation for the observation that $ZnCl_4^{2-}$ undergoes the same slight shift in ν_1 on dissolution as do $ZnBr_4^{2-}$ and ZnI_4^{2-} is that the first complex also retains its tetrahedral coordination.

Acknowledgment.—This work was supported by the National Science Foundation, under Grant GP 3404.

[11] M. L. Delwaulle, *Compt. Rend.*, **238**, 2522 (1954).

[12] T. G. Spiro, *Inorg. Chem.*, **4**, 1290 (1965).

[13] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 106.

[14] Reference 13, p 119.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE
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Substituted Halocarbonyl Complexes of Rhenium(I) with Ligands Having Oxygen as the Donor Atom

BY UGO SARTORELLI, FRANCO CANZIANI, AND FRANCO ZINGALES

Received May 3, 1966

The first replacement reaction of carbon monoxide on metal carbonyls with ligands having oxygen as donor atom has been done in our laboratories by allowing molybdenum and tungsten hexacarbonyls to react with tertiary phosphine oxides.[1]

Hieber and co-workers[2] in the reaction of $H_3Mo_2(CO)_6(OH)_3$ with triphenylphosphine oxide obtained a compound which they considered $Mo(CO)_3(C_6H_5)_3$-

[1] F. Canziani, F. Zingales, and U. Sartorelli, *Gazz. Chim. Ital.*, **94**, 841 (1964).

[2] W. Hieber, K. Englert, and K. Rieger, *Z. Anorg. Allgem. Chem.*, **300**, 295 (1959).