We conclude that although it may be possible to prepare salts of $[ReCl_6]^{3-}$ under suitable conditions, the existing claim[5] to such a preparation is invalid.

All pressure reactions were carried out in Pyrex glass tubes contained in steel bombs using an autoclave rocking unit.

Ammonium perrhenate (0.02 *M*) and ammonium chloride (0.04 *M*) in concentrated hydrochloric acid (40 ml.) were heated for 1.5 hr. with hydrogen at 150° and an initial pressure of 100 atm. The products, large green octahedra, red-brown octahedra, and small yellow crystals, were filtered, washed with concentrated hydrochloric acid and ethanol, and dried under vacuum.

Using identical conditions, potassium perrhenate (0.002 *M*) and potassium chloride (0.004 *M*) in concentrated hydrochloric acid (5 ml.) yielded large green octahedra and small yellow crystals.

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The Infrared Spectra of Ammines of Cobalt(III) Chloride

Sir:

Use of infrared spectra in the 700–200 cm.$^{-1}$ region to establish the identity of certain thermal decomposition products of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and *trans*-$[Co(NH_3)_4Cl_2]Cl$[1] has led to a re-examination of the spectra of these three ammines[2] and a re-evaluation of the assignments previously proposed for absorptions in the CsI region.[3] While our spectral data are in generally good agreement with those of Shimanouchi and Nakagawa,[4] we believe that their conclusions with regard to the Co–X and Co–N stretching vibrations require reconsideration.

In their study of the spectra of $[Co(NH_3)_6]X_3$ ($X = Br^-, I^-$), $[Co(NH_3)_5X]^{2+}$ ($X = F^-, Cl^-, Br^-, I^-$), and *trans*-$[Co(NH_3)_4X_2]^+$ ($X = Cl^-, Br^-$), Shimanouchi and Nakagawa assumed that the NH_3 ligand behaved as a dynamic group. This permitted a normal coordinate analysis of these systems and allowed the mathematical treatment to be that of a seven-body problem. As a result, interactions (coupling) between the low frequency (below 900 cm.$^{-1}$) vibrations of NH_3 and the Co–N skeleton had to be ignored or assumed negligible; this would appear to be an unsupported condition.

With regard to the Co–X stretching mode, Shimanouchi and Nakagawa calculated the following stretching force constants (mdynes/Å.): *K*(Co–F), 2.00; *K*(Co–Cl), 1.97; *K*(Co–Br), 2.53; and *K*(Co–I), 2.00. For $[Co(NH_3)_5X]^{2+}$ these data require assignment of the Co–X stretching mode as follows: F^-, 504 and 493 cm.$^{-1}$; Cl^-, 487 and 479 cm.$^{-1}$; Br^-, 487 cm.$^{-1}$; and I^-, 428 cm.$^{-1}$. That the Co–X bond order should follow the trend Co–Br, Co–I, Co–Cl[5] is subject to question on the basis of a simple electronegativity argument that is supported by recent nuclear quadrupole resonance studies of metal–halogen complexes[6] and a far-infrared spectral study of tetrahalometalates.[7] Data from the latter reference show that the bond order is not Co–Br, Co–I, Co–Cl, but rather Co–Cl, Co–Br, Co–I as expected. Also, there is no apparent reason for two absorption bands for the single nondegenerate Co–X stretching motion in $[Co(NH_3)_5X]^{2+}$, except the possibility of lattice coupling, in view of the reported crystal structure[8] of $[Co(NH_3)_5Cl]Cl_2$.[9] Recent work[7,10,11] on the Co–Cl stretching mode in $[CoCl_4]^{2-}$ led to assignments which, together with data on Pd–Cl and Pt–Cl stretching motions,[12] lead us to the conclusion that the 290 cm.$^{-1}$ band in $[Co(NH_3)_4Cl_2]Cl$, and the 283 cm.$^{-1}$ band in $[Co(NH_3)_5Cl]Br_2$ and $[Co(NH_3)_5Cl](NO_3)_2$, are due to the Co–Cl stretching vibration. Accordingly, it must follow that the Co–Br and Co–I modes lie below 250 cm.$^{-1}$, which is supported by the recent work of Sabatini and Sacconi.[7]

With regard to the Co–N stretching vibrations, Shimanouchi and Nakagawa assigned the (Co–N) F_{1u} stretching mode in $[Co(NH_3)_6]^{3+}$ at 464 cm.$^{-1}$. Both they and Nakamoto, *et al.*, have published spectra for $[Co(NH_3)_6]I_3$ that are somewhat different,[4,13] and the spectra obtained by the latter for $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]Br_3$, and $[Co(NH_3)_6]I_3$ focus attention on the crystal structure of each complex and the three weak bands at 450–500 cm.$^{-1}$. The chloride and bromide are monoclinic and the iodide is cubic.[14] The space group for the iodide is O_h^5-$F4/m\bar{3}2/m$, with $Z = 4$. Hence the Co^{3+} ion in $[Co(NH_3)_6]^{3+}$ resides at a lattice site of O_h symmetry, and therefore the selection rules operative are those associated with the O_h point group.[15-17] Thus, if the three weak bands observed for the chloride and bromide are the com-

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(1) G. W. Watt, *Inorg. Chem*, **3**, 325 (1964).

(2) Measured as Nujol mulls using a Beckman IR-7 infrared spectrophotometer in conjunction with a Beckman long wave length (CsI) interchange.

(3) For review and references see: K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 143–151.

(4) T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).

(5) The Co–F case is not compared in view of its recognized anomalous behavior.

(6) D. Nakamura, K. Ito, and M. Kubo, *Inorg. Chem.*, **2**, 61 (1963), and pertinent references therein cited.

(7) A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

(8) Y. Shigeta, Y. Komiyama, and H. Kuroya, *Bull. Chem. Soc. Japan*, **36**, 1159 (1963).

(9) Crystalline $[Co(NH_3)_5Cl]Cl_2$ is orthorhombic, having a CaF_2-type lattice. The space group is Pnma-D_{2h}^{16}, with $Z = 4$, thus placing the $[Co(NH_3)_5Cl]^{2+}$ in general positions.

(10) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

(11) R. J. H. Clark and T. M. Dunn, *ibid.*, 1198 (1963).

(12) E. G. Brame, Jr., Dissertation, University of Wisconsin, 1957.

(13) K. Nakamoto, Y. Morimoto, and J. Funito, Proceedings of the 7th International Conference on Coordination Chemistry, Almqvist & Wiksell, A.B., Uppsala, Sweden, 1962, pp. 14–16.

(14) M. Gimenez-Huguet, *Dissertation Abstr.*, **22**, 2209 (1962).

(15) R. S. Halford, *J. Chem. Phys.*, **14**, 8 (1946).

(16) H. Winston and R. S. Halford, *ibid.*, **17**, 607 (1949).

(17) D. F. Hornig, *ibid.*, **16**, 1063 (1948).

ponents of the F_{1u} species, which have been split owing to the monoclinic environment, then a single band of reasonable intensity would be expected in the spectrum of the iodide. According to Nakamoto, *et al.*, this is not the case, and the spectrum obtained by Shimanouchi and Nakagawa therefore imposes an indeterminate answer.

In view of these uncertainties, we suggest that the nature of the Co–N stretching and deformation modes remains to be resolved. We plan to observe the spectra of appropriate complexes below 200 cm.$^{-1}$ and undertake a complete (as possible) normal coordinate analysis.

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Book Reviews

Chromatographic Methods. By R. STOCK and C. B. F. RICE, Department of Chemistry and Biology, College of Technology, Liverpool. Chapman and Hall Ltd., 37 Essex Street, London W. C. 2. 1963. viii + 206 pp. 13.5 × 21.6 cm. Price, 40 s.

The importance of chromatography to chemistry is readily apparent from its phenomenal growth and widespread use. There are many books that deal with special types of chromatography, but considerably fewer that attempt to cover the spectrum. The appearance of a book with such a general title, therefore, might be expected to elicit interest from several sectors. This book is an introductory treatment of chromatography, with primary emphasis on techniques. It is intended principally for advanced undergraduates, but will also be of value to chemists who want an introduction to the chromatographic techniques with which they are unfamiliar.

The first chapter gives a short and excellent classification of chromatographic processes and an introduction to the principles of chromatography. Partition and adsorption methods are compared and the advantages of each discussed. After classifying the techniques according to phenomenon, *i.e.*, adsorption *vs.* partition, and giving a breakdown depending on the physical states of the stationary and mobile phases, the authors choose in the remainder of the book to discuss the topics according to similarities in techniques. In Chapter 2, for example, they discuss all types of liquid-phase column chromatography including liquid–solid, liquid–liquid, and ion-exchange processes.

The longest and most detailed chapters deal with paper and gas chromatography. The chapter on paper chromatography presents methods of development (ascending, descending, and horizontal), selection and preparation of solvent and paper, and methods of detection and identification of the separated components. In the same chapter there are brief discussions of thin-layer chromatography and zone electrophoresis. The latter, though not strictly a chromatographic method, was included because the techniques are closely related to those in paper chromatography. In the chapter on gas chromatography, the section entitled "Inorganic Separations" will be of special interest to the inorganic chemist. The number and variety of studies reported is indicative of the recent intense research in inorganic applications of gas chromatography. The first portion of the chapter is devoted to a description of techniques and apparatus, and at the end of the chapter there is a discussion of the theory of chromatography. The placement of this all-important section at the end of the next to the last chapter could be criticized. It would have been better to present the discussion earlier.

On the whole, the explanations are clear, but an exception is found on p. 141 where the limitation of gas chromatography to volatile samples is discussed. It is correctly stated that the vapor pressure of substances to be separated need only be a few millimeters, but the accompanying explanation implies that the ease of elution is a function of the sample size.

The last chapter describes eighteen model experiments based on the authors' experience in teaching a course on chromatography. The experiments were chosen to give an example of each of the main procedures and demonstrate the principles involved. There are frequent references to earlier discussions that are germane to the various experiments. For reasons of simplicity, paper chromatographic experiments are the most numerous. There are two experiments in gas chromatography that merit special comment. For the laboratory without gas chromatography equipment, the authors have thoughtfully described a simple apparatus, attributed to Cowan and Sugihara, which can be quickly assembled from glass tubing and cleverly makes use of the eye as a detector. A second experiment requires a conventional apparatus of the type now available in most laboratories. The student is asked to perform a variety of separations and to determine the efficiency of the column by measurement of HETP values.

Aside from the minor objections noted earlier, the book is written clearly and concisely. It is well referenced at the end of each chapter and has a valuable bibliography following the Appendix. The volume gives an excellent treatment of the practical aspects of chromatography and will be welcomed as a teaching aid. It must be recognized, however, as introductory in scope; therefore it will be necessary for those anticipating the use of chromatography in their research to supplement their reading by reference to more comprehensive works.

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The Constitution of Glasses. A Dynamic Interpretation. Volume I. By WOLDEMAR A. WEYL and EVELYN CHOSTNER MARBOE. Interscience Publishers, 440 Park Avenue South, New York 16, N. Y. 1962. xix + 427 pp. 15 × 23 cm. Price, $16.00.

Volume I of this two-volume series is subtitled "Fundamentals of the Structure of Inorganic Liquids and Solids." In keeping with this subtitle, some ten or eleven of its sixteen chapters are devoted to a summary of the properties of condensed systems in general and a discussion of forces and bonding in such systems. The remaining chapters deal with the glassy state, its formation and constitution, and experimental approaches to studying constitution. The discussions are documented by some 300 references. Both an extensive author index and a somewhat abbreviated subject index are included.

The book is substantially a presentation of a case for a dynamic approach to glass formation as opposed to the structural approach that stems from the classic studies of Zachariasen. To this end, much emphasis is laid upon an electrostatic approach to bonding in terms of extensions of the Fajans quanticule approach and in-