

transitions—necessarily optically active—which are hidden even in the absorption spectrum itself.

On other occasions, O.R.D. measurements have afforded valuable information which could not have readily been culled from present C.D. data. The very tailing of the O.R.D. curves which has been cited as a disadvantage in the preceding discussion can be turned to excellent advantage<sup>7,8</sup>: the presence of high-intensity Cotton effects lying in wave length regions which are at present spectropolarimetrically and spectrodichrometrically inaccessible (“invisible giants”) can often be easily and unequivocally inferred by an examination of the long-wave length O.R.D. region. For example, it had previously been noted<sup>6,7</sup> that background rotations from a curve centered at short wave lengths is superimposed on all but one of the O.R.D. curves of simple six- and seven-membered ring bridged 1,1'-binaphthyls and 2,2'-dimethyl- and 2,2'-dichlorobiphenyls.<sup>11</sup> This curve dominates the whole visible region and is opposite in sign to that of the interposed conjugation band Cotton effect at 240–245 m $\mu$  and the binaphthyl band Cotton effects in the 250–330 m $\mu$  region. The position (*i.e.*, below 220 m $\mu$  for the biphenyls and below 240 m $\mu$  for the binaphthyls) and the sign of this high-amplitude Cotton effect had been clearly discerned in the O.R.D. study. In fact, so dominant is the background rotation in the visible due to this Cotton effect that a fairly

(11) It is not unlikely that the background rotation in the case of the one exception (compound XXI in the present study) also makes a weak contribution to the O.R.D. in the visible region, but it has not thus far been possible to demonstrate such an effect experimentally.<sup>5</sup>

successful correlation of sign of rotation at the sodium D-line and absolute configuration in the biphenyl series (the Bridge rule) had at one time been established.<sup>9,11</sup> By contrast, in the C.D. study only compound XXXV clearly displays a short-wave length maximum, while compounds XXIV and XXV show bare intimations of this effect.

A judicious use of both C.D. and O.R.D. information is therefore clearly indicated. Present instrumentation dictates that “invisible giants” are best detected by O.R.D. measurements since their Cotton effects are felt as background curves and frequently even as the dominant effect of optical rotatory power in the region under investigation. On the other hand, C.D. is most useful in identifying relatively weak optically active transitions, especially in the longer wave length region where their presence may be obscured in both absorption and O.R.D. spectra by broad, overlapping neighboring bands.

### Experimental

Circular dichroism measurements were conducted in the solvents presented in Table I using a Baird-Atomic/Jouan Dichrograph (model JO-1). The concentrations employed (Table I) were such as to maintain the slit width below 1.3 mm. in the region of the circular dichroism maximum. The molecular ellipticity  $[\theta]$  is expressed<sup>1</sup> as  $[\theta] = 2.303(4500/\pi)(\epsilon_L - \epsilon_R)$  with  $(\epsilon_L - \epsilon_R) = d \times \text{sensitivity} \times 10^{-4} \times \text{mol. wt.}/c \times l$ , where  $d$  is the recorder deflection (in mm.) at the particular sensitivity setting (1.5, 2 or 3) of the instrument,  $c$  is the concentration in g./l. and  $l$  is the cell path length in cm.

Pertinent absorption spectra were obtained using an Applied Physics Corporation model 14 spectrophotometer.

---

## COMMUNICATIONS TO THE EDITOR

---

### THE METAL-METAL BONDED, POLYNUCLEAR COMPLEX ANION IN CsReCl<sub>4</sub>

Sir:

We present here a brief preliminary report of a recently determined structure which we believe provides a key to understanding various aspects of the chemistry of rhenium in its +3 oxidation state and probably has important implications regarding the chemistry of some other heavy transition elements.

Despite its rather innocent looking formula, CsReCl<sub>4</sub> was found to have a large orthorhombic unit cell ( $a = 14.06 \text{ \AA.}$ ,  $b = 14.00 \text{ \AA.}$ ,  $c = 10.69 \text{ \AA.}$ ) containing twelve of the above formula units. The possibility of an unexpectedly complicated structure thus was suggested at a very early stage. From systematic absences, the possible space group could be limited to Cmc<sub>2</sub>m, Cmc<sub>2</sub>i, and Ama2. By conventional statistical treatment<sup>1</sup> of the distribution of intensities in the principal zones, the last space group (a non-centric one) was unambiguously indicated. A positive piezoelectric test and the complete success of the ultimate refinement of the structure leave no doubt that this choice is correct.

Using some 580 reflections, a three-dimensional Patterson synthesis was computed and rhenium and cesium positions were eventually established by semi-systematic use of minimum functions of several ranks.<sup>2</sup> Using only these heavy atoms for phasing, a structure factor calculation was made giving a discrepancy index,  $R$ , of only 35%, thus indicating the probable correct-

ness of the heavy atom coordinates. One cycle of least squares refinements then was run varying all parameters and a Geller correlation matrix constructed. This showed several strong parameter interactions and refinement thus was continued allowing only those parameters which did not interact strongly to vary simultaneously. Ten such cycles reduced  $R$  (for Re and Cs only) to 18%. A difference Fourier map, in which the heavy atoms were subtracted out, revealed the chlorine positions quite clearly. After a number of cycles of full-matrix, least squares refinement, the discrepancy index had dropped to 7.3%, and a difference Fourier synthesis showed no anomalies.

The structure of the complex anion is shown in perspective in Fig. 1. Some of the important bond lengths (in Angstroms) and bond angles (in degrees), with estimated standard deviations in parentheses, are

$$\begin{aligned} \text{Re}_1\text{-Re}_{11} &= \text{Re}_{11}\text{-Re}'_{11} = 2.47 (0.01) \\ \text{Re-Cl (bridging)} &= 2.39 (0.03) \\ \text{Re-Cl (out of plane)} &= 2.36 (0.03) \\ \text{Re-Cl (in plane)} &= 2.52 (0.03) \\ \text{Cl}_7\text{-Cl}_5 &= \text{Cl}_7'\text{-Cl}_5 = \text{Cl}_7\text{-Cl}_7' = \text{Cl}_6\text{-Cl}_8, \text{ etc.} = 3.28 (0.06) \\ \langle \text{Cl}_2\text{Re}_{11}\text{Cl}_4 \rangle &= \langle \text{Cl}_2\text{Re}'_{11}\text{Cl}_4' \rangle, \text{ etc.} = 91^\circ (1.0) \\ \langle \text{Cl}_3\text{Re}_1\text{Cl}_3 \rangle &= \langle \text{Cl}_3\text{Re}_1\text{Cl}_3 \rangle, \text{ etc.} = 79^\circ (1.0) \end{aligned}$$

While the  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  ion is required crystallographically to have only one plane of symmetry (passing through  $\text{Re}_1$  and bisecting the  $\text{Re}_{11}\text{-Re}'_{11}$  line) it actually exhibits  $D_{3h}$  symmetry within experimental uncertainties. Hence, only the mean values of the various types of Re-Cl distances are quoted above.

The five chlorine atoms bound to each rhenium atom lie approximately at five of the apices of an octahe-

(1) E. R. Howells, D. C. Phillips and D. Rogers, *Acta Cryst.*, **3**, 210 (1950).

(2) M. J. Buerger, "Vector Space," John Wiley and Sons, Inc., New York, N. Y., 1961.

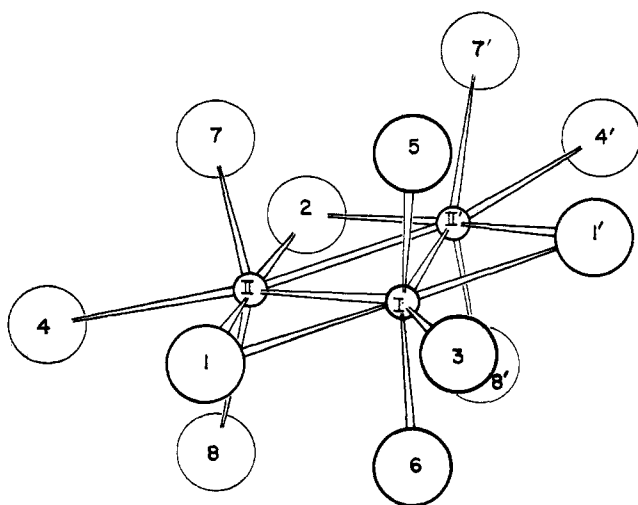


Figure 1.

dron about the rhenium, the chief deviations being in the angles of only  $\sim 79^\circ$  made by the Re-Cl (out of plane) bonds with the  $\text{Re}_3$  plane. This is readily attributable to van der Waals repulsions. The Re-Cl (in plane) distances are decidedly long (2.52), while the other two types of Re-Cl bonds are of about normal length for single bonds.

The very short Re-Re distances are of great interest. They indicate that, while the bridging chlorine atoms may play a role in holding the triangular array of rhenium atoms together, there is strong metal-metal bonding.<sup>3</sup> It appears that a satisfactory first-order treatment of the metal-metal bonding can be given using an LCAO-MO approach. Each rhenium atom is taken to form a set of hybrid, octahedrally directed  $\sigma$  orbitals, of which five are used to bind chlorine atoms and the sixth points to the center of the triangle. These then combine to form a bonding ( $A'$ ) and an antibonding ( $E'$ ) MO. Similarly, the  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals of each rhenium atom combine to give bonding and antibonding, 3-center MO's. There are just six bonding orbitals which are filled by the twelve electrons, thus accounting for the experimentally observed diamagnetism. The structure and bonding in  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  have been found to exhibit certain striking similarities to what is found in the  $[\text{Mo}_6\text{X}_8]^{4+}$  and  $[\text{M}_6\text{X}_{12}]^{2+}$  systems<sup>3</sup>; these relationships will be discussed separately.<sup>8</sup>

The structure of the  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  ion leads to the consideration of some related plausible structures for some other  $\text{Re}^{\text{III}}$  complexes. For example, the compounds<sup>9-11</sup>  $\text{ReLCl}_3$  ( $L = \text{py}$ ,  $(\text{C}_6\text{H}_5)_3\text{P}$  or  $(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2\text{P}$ ) seem likely to have similar trimeric structures in which the three in-plane  $\text{Cl}^-$  ions are replaced by the neutral ligands  $L$ .  $\text{ReCl}_3$  has long been known<sup>12</sup> to give

(3) In rhenium metal, the Re-Re distances are 2.74 and 2.76 Å.<sup>4</sup> In the polynuclear cations,  $[\text{Mo}_6\text{Cl}_8]^{4+}$ ,  $[\text{Nb}_6\text{Cl}_{12}]^{2+}$ ,  $[\text{Ta}_6\text{Cl}_{12}]^{2+}$  and  $[\text{Ta}_6\text{Br}_{12}]^{2+}$ , which contain octahedra of metal atoms,<sup>5</sup> the metal-metal distances are, respectively, 2.63, 2.85, 2.90 and 2.90 Å. In  $\text{Os}_3(\text{CO})_{12}$  the Os-Os distances<sup>6</sup> are  $2.88 \pm 0.01$  Å. Comparison with these data would indicate that the Re-Re bonding in  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  must be quite strong. Pauling<sup>7</sup> predicts a distance of  $\sim 2.56$  Å. for a Re-Re single bond.

(4) C. T. Sims, C. M. Craighead and R. I. Jaffee, *J. Metals*, **7**, 168 (1955).

(5) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 440.

(6) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

(7) Reference 5, p. 403.

(8) T. E. Haas and F. A. Cotton, to be published.

(9) M. Freni and V. Valenti, *Proc. Intern. Cong. Pure Appl. Chem.*, 17th, Munich, 1959, Abstract A1057.

(10) R. Colton, R. Levitus and G. Wilkinson, *J. Chem. Soc.*, 4121 (1962).

(11) J. Chatt and G. A. Rowe, *ibid.*, 4019 (1962).

(12) N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford, 1950, p. 1313. There is a report that the material is polymeric in solution, though it is claimed that it is a dimer rather than a trimer as we

aqueous solutions which, when freshly prepared, contain insufficient free  $\text{Cl}^-$  ion to afford a precipitate with  $\text{Ag}^+$ . Such solutions might contain  $\text{Re}_3\text{Cl}_9(\text{H}_2\text{O})_3$  species in which the in-plane  $\text{Cl}^-$  ions of  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  have been replaced by  $\text{H}_2\text{O}$ . One final example of the possible significant implications of the structure reported here, this relating to a compound of a different heavy metal, is the possibility that the reported compound<sup>13</sup>  $\text{K}_3\text{W}_3\text{Cl}_{14}$  is in fact  $\text{K}_3\text{W}_3\text{Cl}_{12}$ , containing a  $[\text{W}_3\text{Cl}_{12}]^{6-}$  ion, isoelectronic and isostructural with the  $[\text{Re}_3\text{Cl}_{12}]^{3-}$  ion ( $\text{W}^{\text{II}}$  and  $\text{Re}^{\text{III}}$  are isoelectronic). These and various other possible inferences from the  $\text{Cs}_3[\text{Re}_3\text{Cl}_{12}]$  structure are under active investigation in this Laboratory.

**Acknowledgment.**—The generous support of this work by the National Science Foundation is gratefully acknowledged.

might suppose. Any partial decomposition or impurities would tend to give a low molecular weight as obtained by measurements of colligative properties.

(13) R. A. Laudise and R. C. Young, *J. Am. Chem. Soc.*, **77**, 5288 (1955). The authenticity of the formula previously given is dubious, because the levels of the impurities,  $\text{K}_3\text{W}_2\text{Cl}_9$  and  $\text{KCl}$ , were so great that they were evident even in powder X-ray photographs.

(14) Fellow of the Alfred P. Sloan Foundation.

DEPARTMENT OF CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE 39, MASS.

J. A. BERTRAND  
F. A. COTTON<sup>14</sup>  
W. A. DOLLASE

RECEIVED MARCH 16, 1963

#### THE IMPORTANCE OF GROUND STATE SOLVATION IN THE SOLVOLYSIS OF *t*-BUTYL CHLORIDE<sup>1,2</sup>

Sir:

We wish to report direct calorimetric measurements of the partial molal heats of solution ( $\Delta\bar{H}_s$ ) for *t*-butyl chloride and several other compounds in a series of aqueous ethanol solutions. A number of authors<sup>3-6</sup> have observed sharp minima in  $\Delta H^*$  for  $\text{S}_{\text{N}}1$  solvolyses of several substrates in aqueous binary solvents between 0.6 and 0.95 mole fraction water. Our results show clearly that for the solvolysis of *t*-butyl chloride in aqueous ethanol at least 95% of the variation of  $\Delta H^*$  in the region of the minimum<sup>3</sup> can be accounted for by changes in ground state solvation leaving transition state changes negligible.

Activation parameters for reactions in solution are defined as the differences in free energy, enthalpy or entropy between the solvated ground state and solvated transition state. There is no way of deciding how much of the variation of  $\Delta H^*$  or  $\Delta S^*$  should be ascribed to changing solvation of either state until standard enthalpies and entropies of solution for ground states are measured in each solution for which activation parameters are known; the sum of the two then by definition will give the thermodynamic properties for the transition state.<sup>3,7,8</sup> It usually is suggested that the needed data for  $\Delta\bar{H}_s$  and  $\Delta\bar{S}_s$  should be obtained from the temperature coefficient of the Henry's law constant ( $\Delta\bar{F}_s^0$ ). As compared with direct calorimetric measurement this requires a prohibitive amount of labor, is inherently less accurate and may be experimentally impractical in cases (such as that discussed

(1) Solvent Effects in Organic Chemistry I.

(2) This work was supported by National Science Foundation Grant G-14583. We are most appreciative of this assistance.

(3) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).

(4) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 931 (1956).

(5) J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 5129 (1960); **84**, 2914 (1962).

(6) E. Tommila, *et al.*, *Acta Chem. Scand.*, **9**, 975 (1955); **6**, 844 (1952); **9**, 989 (1955); *Ann. Acad. Sci. Fennicae, Ser. A*, **II**, No. 65 (1955), and other papers.

(7) R. A. Clement, J. N. Naghizadeh and M. R. Rice, *J. Am. Chem. Soc.*, **82**, 2449 (1960).

(8) R. E. Robertson, R. L. Heppollette and J. M. W. Scott, *Can. J. Chem.*, **37**, 803 (1959).