cation was much simpler than that for products of the classical preparations. Yields were 60% of the theoretical amount, which is about the same as those obtained by the more tedious classical procedures. However, when the reaction is run in the "chloride mixture" as reported here the yield is approximately 20% better than when the chloride is not present. In addition, the reaction occurs at temperatures low enough so that the reaction can be run in a 1-l. round-bottom flask in an ordinary heating mantle. This modification of Johannesen's procedure represents a significant improvement in the method for the preparation of vanadium oxytrichloride. The procedures reported here do not have any advantages over the conventional ways of preparing the other volatile halides reported in this article.

It is of interest to generalize about these reactions to aid in the extension of the reactions to other systems. The reactions of aluminum chloride with oxides to form acid chlorides may be formulated generally as

$$EO_m + nAlCl_3 \longrightarrow EO_xCl_y + {}^{n}/_{2}Al_2O_3 \qquad (1)$$

where E is the general symbol for an element. Undoubtedly, these formulations of the reactions are greatly oversimplified and the actual products may be various aluminum oxychlorides. The reactive aluminum-containing species is also unknown. It may be $AlCl_3$ or a cationic chloroaluminum complex. The chloride atoms which appear in the volatile acid chlorides likely come from the solvent rather than from aluminum chloride molecules or any chloroaluminum complex species. The greater concentration of chloride ion and the anticipated greater nucleophilicity of this species compared with the tetrachloroaluminate ion suggest this. Of course, rapid exchange of all chloride in this system is expected and eventual displacement of chloride from aluminum by oxide is indicated in eq 1. Two mechanisms which conveniently explain the experimentally observed facts can be proposed. One is an ionic mechanism in which the chloroaluminum species coordinates with an oxygen-containing species through the oxygen. The resulting complex is sufficiently polarized that the bond between the central element and the oxygen which is coordinated to the aluminum is broken, leaving a cationic species. This cation could then combine with one or more chlorides from the solvent to form the volatile oxychloride molecule. A second possibility would be an $S_N2$ mechanism, in which a neutral $AlCl_3$ molecule or a cationic chloroaluminum species could coordinate with an oxygen of an oxide or oxyanion. This could result in polarization of the central element–oxygen bond, so that a chloride ion could attack the relatively positive central element and an oxide ion could be displaced. When a cation is formed by displacement of oxygen by chlorine, additional chloride can be obtained from the solvent to form the volatile nonmetal halide.

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# Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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## The Lattice Energy of Sodium Tetrachloroaluminate and the Heat of Formation of the Tetrachloroaluminate Ion[1]

BY R. H. WOOD AND L. A. D'ORAZIO

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In the past, most of the work on the interaction energies of donor–acceptor complexes has been limited to complexes with no net charge.[2] This restriction has been imposed by the difficulty of calculating lattice energy effects in solids and solvent effects in solutions. In the last few years, however, machine computation of electrostatic energies has been achieved, and lattice energy effects have become easily calculable.[3,4] The present paper reports the results of applying the crystal lattice energy calculation to the determination of the energy of the aluminum chloride–chloride ion complex.

### Calculation of the Madelung Constant

The Madelung constant of $NaAlCl_4$ was calculated by the method of Wood[3a,5] for the crystal structure proposed by Baenziger.[6] He reports the symmetry[7] as $P2_12_12_1$ with $a$ = 10.36, $b$ = 9.92, and $c$ = 6.21. The coordinates of the different kinds of atoms have been given by Baenziger.

The Madelung constant was calculated for the process

$$NaAlCl_4(c) \longrightarrow Na^+(g) + AlCl_4^-(g)$$

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[1] This study was supported by the Air Force Office of Scientific Research Grant No. AF-AFOSR-325-63.

[2] Reviews of several aspects of this subject are given in the chapters by R. J. Gillespie, M. Baaz and V. Gutman, D. R. Martin and J. R. Cannon, and N. N. Greenwood and K. Wade in "Friedel-Crafts and Related Reactions," G. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

[3] (a) R. H. Wood, *J. Chem. Phys.*, **32**, 1690 (1960); (b) Q. C. Johnson and D. H. Templeton, *ibid.*, **34**, 2004 (1961).

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[5] The authors thank the Computing Center of the University of Delaware for the use of their facilities.

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assuming three different charge distributions for the tetrachloroaluminate(III) ion. The charge distributions are: +3.0 charge on the aluminum atom and −1.0 charge on each chlorine atom (case I), −0.2 charge on the aluminum and each chlorine (case II), and −1.0 charge on aluminum and zero charge on the chlorine atoms (case III). In cases I and II the unit cell had a net dipole moment so that corrections of 0.06 and 0.02%, respectively, were necessary.[8] The results of the calculations are given in Table I. The contribution of the fourth shell of unit cells in case III (0.03%) is taken as an estimate of the accuracy of the calculation in cases I and II.

TABLE I

MADELUNG CONSTANT FOR $NaAlCl_4$

| | Charge distribution | $M_\delta(Na[AlCl_4])$ | 3rd shell contribution | 4th shell contribution |
|---|---|---|---|---|
| Case I | $Na^+(Al^{+3}Cl^-{}_4)^-$ | 2.4055 ± 0.03% | 0.2% | |
| Case II | $Na^+(Al^{-0.2}Cl^{-0.2}{}_4)^-$ | 2.1782 ± 0.03% | 0.4% | |
| Case III | $Na^+(Al^-Cl^0{}_4)^-$ | 2.1605 ± 0.03% | 0.5% | 0.03% |

The Madelung constant for any other charge distribution can be calculated using the information that the constant is at most a quadratic function of the charge. This is easily shown by considering the individual sums in the calculation.[3]

## Calculation of the van der Waals Energies

The van der Waals (dispersion) energy has been calculated from the Slater and Kirkwood equation[9]

$$U_v = \frac{3eh}{4\pi m^{1/2}R^6}\,\frac{a_A a_B}{\left(\dfrac{a_A}{N_A}\right)^{1/2} + \left(\dfrac{a_B}{N_B}\right)^{1/2}} = \frac{C_{AB}}{R^6}$$

The interaction constants ($C_{AB}$) for sodium and chloride ions have been taken directly from Mayer.[10] The interaction constants involving aluminum ions have been calculated from Pauling's value for the polarizability[11] ($\alpha_{Al^{+3}} = 0.052 \times 10^{-24}$ cm$^3$) and an estimate of the number of effective electrons ($N_{Al^{+3}} = 5.15$). The value for $N_{Al^{+3}}$ was estimated from the values for sodium and fluoride ions by assuming a linear variation between $N^{1/2}$ and nuclear charge. $N^{1/2}$ for the sodium and fluoride ions was calculated from Mayer's values for their interaction constants and the Slater–Kirkwood formula. This procedure is equivalent to that used by Huggins and Sakamoto[12] in their estimation of the van der Waals energies for the alkaline earth chalcogenides. The results should not be sensitive to the assumption that the complex is ionic since any deviation in the polarizability should be largely balanced by a change in the effective number of electrons. For example, the interaction constants of chloride ion and argon are nearly the same.

The van der Waals sums were calculated as previously described[13] and are given in Table II. The interaction constants are also given in Table II.

TABLE II

VAN DER WAALS SUMS ($S_{AB}$) AND INTERACTION CONSTANTS ($C_{AB}$)

| Interaction | $C_{AB} \times 10^{60}$, ergs cm$^6$ | $S_{AB}$ |
|---|---|---|
| $Na^+$–$Na^+$ | 1.68 | 3.787 |
| $Cl^-$–$Cl^-$ | 120 | 168.834 |
| $Na^+$–$Cl^-$ | 10.0 | 28.242 |
| $Al^{+3}$–$Al^{+3}$ | 0.34 | 4.308 |
| $Al^{+3}$–$Na^+$ | 0.69 | 28.822 |
| $Al^{+3}$–$Cl^-$ | 3.36 | 55.28 |

## Results and Discussion

The lattice energy of $NaAlCl_4$ was calculated by the method of Ladd and Lee.[14] The calculation was made for the hypothetical lattice at 0°K assuming a 1% decrease in the cube root of the molecular volume (*i.e.*, $\delta_{298°K} = 5.4237$ A $\rightarrow \delta_{0°K} = 5.37$ A). The value of the repulsion exponent, $\rho = 0.333$ A, was taken from data on the alkali halides. The results are given in Table III.

TABLE III

LATTICE ENERGY FOR $NaAlCl_4$

| | Case I | Case II | Case III |
|---|---|---|---|
| Coulomb energy, kcal/mole | 148.8 | 134.7 | 133.6 |
| van der Waals energy, kcal/mole | 12.5 | 12.5 | 12.5 |
| Repulsion energy, kcal/mole | −13.9 | −13.0 | −12.9 |
| Lattice energy, kcal/mole | 147.4 | 134.2 | 133.2 |
| $\Delta H_f°(AlCl_4^-,g)$, kcal/mole | | −277 ± 7 (av value) | |

The heat of formation of the gaseous tetrachloroaluminate ion ($\Delta H_f°(g) = -277 \pm 7$ kcal/mole) was calculated from the cycle

$$\Delta H_f°(AlCl_4^-,g) = U + \Delta H_f°(NaAlCl_4,c) - \Delta H_{sub} - IP(Na) + \int_{290}^{0} (C_p(NaAlCl_4,c) + C_p(e^-,g) - C_p(Na,g) - C_p(AlCl_4^-,g))dT$$

The lattice energy ($U = 138 \pm 7$ kcal/mole) was taken as the average of the three cases calculated in Table III. This average corresponds to about 50% ionic character of the bonds (−0.5 charge on the chlorine atoms).

An uncertainty of 7 kcal/mole includes a wide variation in the charge distribution of the $AlCl_4^-$ ion extending from 0 to 90% ionic character of the aluminum chlorine bonds. Certainly, cases I and III which correspond to completely ionic and completely covalent bonding are too extreme. The contribution of possible errors in the crystal structure parameters, the repulsion energy, and the van der Waals energy to the uncertainty in the lattice energy is much smaller.

The heat of formation of $NaAlCl_4$ (270.6 kcal/mole) was taken from Rossini, *et al.*[15] The heat capacity

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[8] For calculating dipole corrections see R. H. Wood and L. A. D'Orazio, *J. Phys. Chem.*, **69**, 2558 (1965).

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[14] See eq 13 of ref 13 and M. F. C. Ladd and W. H. Lee, *J. Inorg. Nucl. Chem.*, **11**, 264 (1959).

[15] F. D. Rossini, *et al.*, National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

terms involving $NaAlCl_4$ and $AlCl_4^-$ (which partially cancel one another) were neglected. From the heats of formation of the gaseous chloride ion (−58.0 kcal/mole) and the gaseous, monomeric aluminum chloride molecule (−140.42 kcal/mole),[16] the dissociation energy of the $AlCl_3–Cl^-$ bond is calculated to be 78 ± 7 kcal/mole.

The heat of breaking a single Al–Cl–Al bridge in $Al_2Cl_6$ is 14.5 kcal/mole[17,18] which is 63 kcal/mole weaker than the $AlCl_3–Cl^-$ bond. This is in accord with the electron diffraction data of Palmer and Elliott,[19] who found that the bond distance of the bridging chloride in $Al_2Cl_6$ (2.21 ± 0.04) was larger than for terminal chlorine in $Al_2Cl_6$ (2.06 ± 0.04) and larger than the Al–Cl distance in the $NaAlCl_4$ (2.13 ± 0.03). Similarly, Klemperer[20] found that the force constants for bridging and terminal chlorines in $Al_2Cl_6$ are approximately 1.3 and 2.5 × $10^5$ dynes/cm, respectively.

The donor strength of the chloride ion toward aluminum chloride as reference acceptor cannot be compared with other donors since the data are lacking. The most extensive series of measurements give only the heat of forming the solid complex,[21,22] and it will be necessary to have many more gas phase heats of complexing before achieving real understanding of the contributions of steric effects and reorganization energy to the bond strength.

[16] B. J. McBride, S. Heimil, J. G. Ehlers, and S. Gordon, "Thermodynamic Properties to 6000°K for 210 Compounds of the First Eighteen Elements," NASA SP-3001, Office of Technical Services, National Aeronautics and Space Administration, Washington, D. C., 1963.

[17] W. Fischer and O. Rahlfs, *Z. Anorg. Allgem. Chem.*, **205**, 1 (1932).

[18] T. G. Dunne and N. W. Gregory, *J. Am. Chem. Soc.*, **80**, 1526 (1958).

[19] K. J. Palmer and N. Elliott, *ibid.*, **60**, 1853 (1938).

[20] W. Klemperer, *J. Chem. Phys.*, **24**, 353 (1956).

[21] D. D. Eley and H. Watts, *J. Chem. Soc.*, 1319 (1954).

[22] D. J. A. Dear and D. D. Eley, *ibid.*, 4684 (1954).

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CONTRIBUTION FROM THE MELLON INSTITUTE,
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# A Tetranuclear Nickel Atom Cluster Derived from Hexafluorobut-2-yne and Nickel Carbonyl[1,2]

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Reactions between hexafluorobut-2-yne ($CF_3C{\equiv}CCF_3$) and several metal carbonyl derivatives have been reported. These studies have resulted in the isolation of the mononuclear hexafluorobutyne complexes $\pi$-$(CF_3)_2C_2Mn(CO)_2(\pi\text{-}C_5H_5)$[5] and $[(\pi\text{-}CF_3)_2C_2]_3W(NCCH_3)$,[6] the binuclear complexes $\pi$-$(CF_3)_2C_2Co_2(CO)_6$ and $\pi$-$(CF_3)_2C_2Ni_2(\pi\text{-}C_5H_5)_2$,[7] the mononuclear tetrakis(trifluoromethyl)cyclopentadienone complexes $[\pi\text{-}(CF_3)_4C_4CO]Fe(CO)_3$,[7] $[\pi\text{-}(CF_3)_4C_4CO]Co(\pi\text{-}C_5H_5)$,[8] and $[\pi\text{-}(CF_3)_4C_4CO]Rh(\pi\text{-}C_5H_5)$[9] and the mononuclear hexakis(trifluoromethyl)benzene complex $[\pi\text{-}(CF_3)_6C_6]Rh(\pi\text{-}C_5H_5)$.[9] We now describe a novel nickel complex $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$.

## Experimental Section

For the preparation of $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ a mixture of tetracarbonylnickel and hexafluorobut-2-yne was heated for about 24 hr at 50° in a sealed evacuated stainless steel reaction vessel.[10] After cooling to room temperature the reaction vessel was opened, and the product was washed out with pentane in small portions, until the originally deep red-purple washings were only weakly colored. After removal of pentane (25 mm), the red-violet residue was sublimed at 50–80° (0.1–0.5 mm) to afford $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$, mp 119–121° dec, exploding in air at 174°. In a typical preparation using a reaction vessel of 150-cc capacity, 13.0 ml (17.2 g, 101 mmoles) of tetracarbonylnickel and 8.0 g (49.4 mmoles) of hexafluorobut-2-yne gave 4.13 g (31% yield) of $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$.

The formula $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ was established most conclusively by high-resolution mass spectrometry (Table I), but was confirmed by elemental analyses.[11]

*Anal.* Calcd for $C_{15}F_{18}Ni_4O_3$: C, 22.4; H, 0.0; F, 42.4; Ni, 29.2. Found: C, 23.2, 22.4; H, 0.3, 0.0; F, 41.7; Ni, 28.5.

The dark purple, pungent-smelling crystals turned brown and became more malodorous upon standing for several days in air. Pentane solutions of the purple solid oxidize in air within several hours, giving a trimer of hexafluorobutyne (parent molecular ion $C_{12}F_{18}^{+}$) as the main volatile component. Degradation of $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ with HCl gas at 40–50° for 46 hr in an evacuated bulb afforded 1,1,1,4,4,4-hexafluoro-2-butene (64% yield), identified by its infrared and mass spectra. As gauged by the color of a pentane solution of $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$, no reaction occurred with triphenylphosphine until three equivalents had been added. At this point the solution immediately decolorized with separation of a pale brown precipitate, which was not characterized.

The infrared spectrum of $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ (cyclohexane solution, high-resolution conditions[12]) showed the following absorptions ($cm^{-1}$) in the regions of interest: $\nu_{CO}$: 2115 (vs), 2103 (vs); $\nu_{C=C}$: 1565 (w), 1550 (w); $\nu_{C-F}$: 1235 (w), 1220 (m), 1205 (s), 1165 (m), 1153 (m). The $^{19}F$ nmr spectrum of $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ exhibited two groups of absorptions of equal intensity at 50.3 and 54.5 ppm, upfield from internal $CCl_3F$ in dichloromethane solutions.

## Discussion

Consideration of a structure for $[\pi\text{-}(CF_3)_2C_2]_3Ni_4(CO)_3$ must be guided by the following requirements: (1) Degradation with hydrogen chloride affords $CF_3CH{=}CHCF_3$, indicating that the $CF_3C{\equiv}CCF_3$ ligands have not condensed to a ring system, as in previously

[1] The initial phases of this work were carried out at Harvard University, Cambridge, Mass., and are described in the Ph.D. thesis (1962) of J. R. Phillips.

[2] The present note constitutes part XXXIV of the series "Chemistry of the Metal Carbonyls" [for part XXXIII see A. Forster, J. B. Wilford, and F. G. A. Stone, *J. Chem. Soc.*, 6519 (1965)] and part XIV of the series "Organometallic Chemistry of the Transition Metals" [for part XIII, see R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966)].

[3] The Mellon Institute, Pittsburgh, Pa.

[4] Department of Inorganic Chemistry, The University, Bristol, U. K.

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[9] R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).

[10] Cylinders (high pressure series) manufactured by Hoke Inc., Cresskill, N. J., were used.

[11] Owing to the presence of carbon, nickel, and especially fluorine, a direct oxygen analysis could not be performed.

[12] J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).