By summing all the above contributions to the covalency, one obtains a total Pt–Cl bond order. This is 0.403 and is almost entirely σ in character. It should be emphasized, however, that the number 0.403 represents the covalency of the Pt–Cl bond. One minus this covalency is, then, the ionicity.

The covalency of the Pt–Cl bond in $PtCl_4^{2-}$ has been measured by nuclear quadrupole resonance (nqr).[32] Marrom, McNiff, and Ragle[33] estimated a covalency of 0.39 and a Pt charge of +0.44 using the usual Townes–Dailey treatment. We calculate a Pt charge of +0.439, using the input parameters of Table V and $K = 1.8$. The agreement is remarkably good, but perhaps open to question due to the assumptions inherent in the application of the Townes–Dailey equation to data.

However, we have recently derived an equation[34] which permits direct calculation of the quadrupole coupling constant and asymmetry parameter from the LCAO–MO eigenvectors and overlap integrals. Using our results for $PtCl_4^{2-}$ we obtain $eQq = 34$ Mc (for ^{35}Cl), compared to the experimental value of 36.1 Mc. Thus, insofar as the charge distribution–covalence criterion is concerned, the present treatment apparently gives very reliable results.

We predict the ^{35}Cl asymmetry parameter, η, equal to 0.072 with the **x** direction of the field gradient tensor perpendicular to the plane of the $PtCl_4^{2-}$ moiety.

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[32] T. P. Das and E. L. Hann, "Nuclear Quadrupole Resonance Spectroscopy, Academic Press Inc., New York, N. Y., 1958.

[33] E. P. Marrom, E. J. McNiff, and J. L. Ragle, *J. Phys. Chem.*, **67**, 1719 (1963).

[34] F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S.*, **56**, 12 (1966).

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Molecular Orbital Calculations for Complexes of Heavier Transition Elements. II. Hexachloro Complexes of Tetravalent Rhenium, Osmium, Iridium, and Platinum[1]

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Extended Hückel calculations, employing the Mulliken–Wolfsberg–Helmholz approximation for the off-diagonal elements of the Hamiltonian matrix, have been carried out for the $ReCl_6^{2-}$, $OsCl_6^{2-}$, $IrCl_6^{2-}$, and $PtCl_6^{2-}$ ions. One of the key features of the procedure was the use of orbital energies for the metal ions very close to those of the uncharged atoms and a very moderated dependence (1 ev/unit charge) of the metal d-orbital energies on effective charge of the metal atom instead of the large (~10 ev/unit charge) dependence which occurs for the free, gaseous metal ions. This moderated dependence is attributable to the molecular environment of the metal ion. A previously described procedure for fitting single Slater-type orbitals to give overlaps practically equal to those obtained with SCF orbital functions was also used. The results obtained are in generally satisfactory agreement with experiment in regard to d-orbital splittings, charge-transfer spectra, and, most particularly, charge distribution and metal–ligand covalence as implied by esr and nqr results. The good agreement in the latter respects is due primarily to the moderated dependence of orbital energy on charge and constitutes good evidence for the reasonableness of this part of the procedure.

Introduction

In the preceding paper[3] a molecular orbital method was developed and applied to the calculation of the molecular properties of $PtCl_4^{2-}$. A method for the interpretation of nuclear quadrupole resonance, based on the principles of molecular orbital theory, has been derived recently[4] and its applicability to the series MCl_6^{2-} (M = Re(IV), Os(IV), Ir(IV), and Pt(IV)) mentioned. This paper provides the details of the MO calculations for this series of complexes and of the application of these MO results to the verification and prediction of molecular properties associated with these molecules. This particular series of complexes was selected because of the opportunity thus provided to examine the effect of a steady increase in the atomic number of the metal ion in a homologous series of complexes for which quadrupole coupling constants are available.

Procedure

The metal 6s, 6p, and 5d atomic orbitals and the Cl 3s and 3p atomic orbitals, a total of 33 wave functions, were used to construct molecular orbitals in the LCAO–MO approximation.[5] All wave functions were expressed as Slater nodeless orbitals[6] using the same method described[3] for treatment of $PtCl_4^{2-}$ to determine the shielding parameters, α_i.

Herman–Skillman radial wave functions[7] were used for the metal 6s and 5d atomic orbitals. The radial portions of the 6p atomic orbitals were approximated

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[1] Work supported by the U. S. Atomic Energy Commission.

[2] Predoctoral Fellow of the National Institutes of Health, 1964–1966; A.E.C. Postdoctoral Fellow, 1966–1967.

[3] F. A. Cotton and C. B. Harris, *Inorg. Chem.*, **6**, 369 (1967).

[4] F. A. Cotton and C. B. Harris, *Proc. Natl. Acad. Sci. U. S.*, **56**, 12 (1966).

[5] J. H. Van Vleck, *J. Chem. Phys.*, **3**, 22 (1934).

[6] J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

[7] F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1963.

TABLE I

MCl_6^{2-} MO INPUT PARAMETERS

Orbital	Atom	Orbital type	Coordinates in A			$ReCl_6^{2-}$		$OsCl_6^{2-}$		$IrCl_6^{2-}$		$PtCl_6^{2-}$	
			X	Y	Z	Orbital exp	H_{ii}	Orbital exp	H_{ii}	Orbital exp	H_{ii}	Orbital exp	H_{ii}
1	1	6s	0.0	0.0	0.0	2.500	−8.67	2.540	−9.50	2.500	−10.33	2.580	−11.16
2	1	$6p_z$	0.0	0.0	0.0	2.200	−4.22	2.240	−5.05	2.200	−5.88	2.280	−6.71
3	1	$6p_x$	0.0	0.0	0.0	2.200	−4.22	2.240	−5.05	2.200	−5.88	2.280	−6.71
4	1	$6p_y$	0.0	0.0	0.0	2.200	−4.22	2.240	−5.05	2.200	−5.88	2.280	−6.71
5	1	$5d_{z^2}$	0.0	0.0	0.0	2.920	−9.48	3.220	−10.31	3.125	−11.14	3.135	−11.97
6	1	$5d_{xz}$	0.0	0.0	0.0	2.920	−9.48	3.220	−10.31	3.125	−11.14	3.135	−11.97
7	1	$5d_{x^2-y^2}$	0.0	0.0	0.0	2.920	−9.48	3.220	−10.31	3.125	−11.14	3.135	−11.97
8	1	$5d_{yz}$	0.0	0.0	0.0	2.920	−9.48	3.220	−10.31	3.125	−11.14	3.135	−11.97
9	1	$5d_{xy}$	0.0	0.0	0.0	2.920	−9.48	3.220	−10.31	3.125	−11.14	3.135	−11.97
10	2	3s	2.360	0.0	0.0	2.200	−23.45	2.200	−23.45	2.200	−23.45	2.200	−23.45
11	2	$3p_z$	2.360	0.0	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
12	2	$3p_x$	2.360	0.0	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
13	2	$3p_y$	2.360	0.0	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
14	3	3s	−2.360	0.0	0.0	2.200	−23.45	2.200	−23.45	2.200	−23.45	2.200	−23.45
15	3	$3p_z$	−2.360	0.0	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
16	3	$3p_x$	−2.360	0.0	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
17	3	$3p_y$	−2.360	0.0	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
18	4	3s	0.0	2.360	0.0	2.200	−23.45	2.200	−23.45	2.200	−23.45	2.200	−23.45
19	4	$3p_z$	0.0	2.360	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
20	4	$3p_x$	0.0	2.360	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
21	4	$3p_y$	0.0	2.360	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
22	5	3s	0.0	−2.360	0.0	2.200	−23.45	2.200	−23.45	2.200	−23.45	2.200	−23.45
23	5	$3p_z$	0.0	−2.360	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
24	5	$3p_x$	0.0	−2.360	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
25	5	$3p_y$	0.0	−2.360	0.0	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
26	6	3s	0.0	0.0	2.360	2.200	−23.45	2.200	−23.45	2.200	−23.45	2.200	−23.45
27	6	$3p_z$	0.0	0.0	2.360	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
28	6	$3p_x$	0.0	0.0	2.360	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
29	6	$3p_y$	0.0	0.0	2.360	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
30	7	3s	0.0	0.0	−2.360	2.200	−23.45	2.200	−23.45	2.200	−23.45	2.200	−23.45
31	7	$3p_z$	0.0	0.0	−2.360	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
32	7	$3p_x$	0.0	0.0	−2.360	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38
33	7	$3p_y$	0.0	0.0	−2.360	1.820	−14.38	1.820	−14.38	1.820	−14.38	1.820	−14.38

as those of the 6s atomic orbitals. Watson–Freeman[8] wave functions were used for the Cl 3s and 3p radial wave functions.

The metal-to-chloride internuclear distance[9] was taken as 2.36 A in all cases, the probable variation from one complex to another being negligible.

The diagonal Hamiltonian matrix elements, H_{ii}, for the metal orbitals were approximated by the valence state ionization potentials (*VSIP*) listed in Table I. Since the spectral assignment of the states listed in Moore's tables[10] is incomplete, we assumed that there is a linear decrease in the *VSIP*'s of analogous orbitals of 2.5 ev going from Re to Pt.[11]

All overlap integrals, S_{ij}, were calculated and all off-diagonal matrix elements, H_{ij}, were approximated by the MWH approximation, $H_{ij} = KS_{ij}(H_{ii} + H_{jj})/2$, with a Helmholz factor, K, equal to 1.80. The secular equations were solved and the MO energies and eigenvectors were determined in each case. For each molecule, the calculation was recycled to a self-consistency within 0.01 charge unit on the metal.

The same dependence of H_{ii} with charge was assumed in these calculations as in the $PtCl_4^{2-}$ MO calculation.[3] That is, instead of the very steep slope of a plot of orbital energy against metal ion charge (of the order of 10 ev/charge unit) which obtains for the ion under vacuum, it is recognized that when the ion is surrounded by the partially negative ligand atoms a much less severe dependence is expected. This point has previously been made by Lohr and Lipscomb,[12] who did not, however, discuss it. More recently Ros[13] has described a procedure for taking account of the effect of the molecular field on the metal orbitals which leads to and hence tends to justify the assumptions that the H_{ii} at the calculated charge are close to those for the uncharged atoms and that a slope, $|d(VSIP)/dq|$, of 1–5 ev/charge unit is reasonable, while the free-ion slopes are far too great. This moderated charge dependence must naturally lead to less equalization of metal and ligand charges and hence to greater metal atom charges. It will be seen, however, that this is in agreement with nqr data.

It should also be noted that when the influence of the field of the ligands upon metal orbital energies is taken fully into account, as in the method Ros,[13] not only is

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(8) R. E. Watson and A. J. Freeman, *Phys. Rev.*, **123**, 521 (1961); **120**, 1125 (1960).

(9) "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

(10) C. E. Moore, "Atomic Energy Levels," U. S. National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949 and 1952.

(11) This somewhat parallels the behavior of the first ionization potentials of the neutral metals.[10]

(12) L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **38**, 1607 (1963).

(13) P. Ros, Thesis, Eindhoven, 1964; P. Ros and G. C. A. Schmit, *Theoret. Chim. Acta*, **4**, 1 (1966).

the charge dependence of the *VSIP*'s altered, but their absolute values are also changed somewhat. This latter effect has been neglected in our calculation. This neglect was deliberate in order to see if merely moderating the charge dependence while using the energy values appropriate to the gaseous neutral atom would provide an adequate but very simple method of improving the results in respect to charge distribution. It appears that this is indeed the case.

All overlap integrals for the Re, Os, Ir, and Pt cases; all eigenvectors for the final cycle; all molecular orbital energies; orbital occupations; and orbital and atomic charges are on file with the American Documentation Institute.[14] Additional numerical results (*e.g.*, overlap populations and bond orders) may be obtained upon request to the authors.

Discussion of Results

Electronic Spectra.—The semiempirical MO theory utilized in these calculations is not well suited for a quantitative description of the electronic spectra because it does not explicitly include electron repulsion integrals in the Hamiltonian. However, it can provide useful information about trends in a given series of related molecules.

Table II lists, *inter alia*, the energies of the last occupied MO's, $\epsilon_{t_{2g}}$; Δ, the separation between the t_{2g} and e_g MO's, and the charge-transfer energies, $t_{2u} \rightarrow t_{2g}$.

TABLE II

MCl_6^{2-} MOLECULAR PROPERTIES

	$ReCl_6^{2-}$	$OsCl_6^{2-}$	$IrCl_6^{2-}$	$PtCl_6^{2-}$
$\epsilon_{t_{2g}}$, ev	−9.98	−10.87	−11.31	−11.83
$t_{2g} \rightarrow e_g$ (Δ), ev	4.91	3.39	4.11	4.30
$t_{2u} \rightarrow t_{2g}$, ev	2.91	2.04	1.65	(1.17)
Metal charge	1.32	1.18	0.89	0.69
Metal–Cl bond order	0.438	0.454	0.475	0.475
σ bond order	0.435	0.445	0.484	0.508
π bond order	0.003	0.009	−0.009	−0.033
% metal in t_{2g} MO	89	90	85	81
eqQ: Calcd	32	38	44	51
Obsd	27.8	33.8	41.6	52.0
Cl occupation				
3s	1.93	1.93	1.91	1.91
$3p_\sigma$	1.68	1.63	1.60	1.54
$3p_\pi$	3.94	3.95	3.96	3.99

The experimental Δ for all members of the series is about 4.1 ev.[15] In view of the sensitivity of the calculated Δ to the values of the variable parameters in this type of calculation (*cf.* ref 3), it is gratifying to obtain an average calculated Δ equal to 4.2 ev.

Although no apparent trend is evident in either the experimental or calculated Δ, there is definitely a trend in the charge-transfer spectra, $t_{2u} \rightarrow t_{2g}$, across the series. Jørgensen[15] has pointed out that the $t_{2u} \rightarrow t_{2g}$ transition generally decreases about 0.75 ev for each new electron in the partly filled t_{2g} molecular orbital with metals of a constant oxidation number. For the particular series of compounds treated in this study the experimental differences[15] in the $t_{2u} \rightarrow t_{2g}$ transition for Re(IV) to Os(IV) and Os(IV) to Ir(IV) are about 0.9 and 0.6 ev, respectively. The calculated differences are in quite satisfactory agreement, being 0.87 and 0.39 ev, respectively.

Charge Distributions and Metal–Chloride Bond Orders.—An important aspect of the results in Table II is the uniform decrease of the effective metal charge in these complexes going from $ReCl_6^{2-}$ to $PtCl_6^{2-}$. A general decrease in charge is qualitatively what one would expect, and nuclear quadrupole resonance (nqr) data[16–18] provide direct evidence for the validity of this trend.

The similarity of the metal–chloride (M–Cl) bond orders or covalencies (Table II) is intriguing when juxtaposed with the effective metal charge decrease. The lack of an appreciable increase in the M–Cl bond order with a substantial metal charge decrease results from the increased occupation of the antibonding t_{2g} MO going across the series. When bond order is reduced to its σ and π contributions, one notes (Table II) a general increase in σ covalency across the series resulting from an electron flow from the Cl $3p_\sigma$ orbitals. This results in decreasing the effective metal charge across the series. However, the antibonding character of the t_{2g} electron added to each member in the series causes a decrease in the M–Cl π-bond order. The inherent symmetry of the π orbitals does not permit them to provide as effective a mechanism for Cl-to-metal charge flow as do the σ orbitals. Consequently, the effective metal charge decreases across the series *via* electron flow from the Cl p_σ orbital. This results in a net increase in σ-bond covalency. Since, however, the t_{2g} MO is an antibonding π-type orbital, there is an increased negative π-bond order across the series. This, to a large extent, cancels out the increased σ-bond order increase resulting in a more uniform total metal–chloride bond order for the compounds listed.

Finally, it is interesting to note that the decrease in the effective metal charge across the series is consistent with the nephelauxetic effect.[19,20]

Spin Densities.—With the exception of $PtCl_6^{2-}$, which has filled t_{2g} MO's, all other complexes in Table II have one or more unpaired electrons. As such, they are subject to esr studies. The only esr study available in the series is that for $IrCl_6^{2-}$.[21] The Cl^{35} hyperfine has been interpreted as arising from a spin density of only 70% on the Ir.[21] The *g* value[21] indicates that about 85% of the spin density is on the Ir.

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[14] A tabulation has been deposited as Document No. 9156 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by an advanced remittance ($2.50 for photoprints or $1.75 for 35-mm microfilm) payable to: Chief, Photoduplication Service, Library of Congress.

[15] C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

[16] D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5783 (1960).

[17] D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *Bull. Chem. Soc. Japan*, **36**, 1056 (1963).

[18] R. Ikeda, D. Nakamura, and M. Kubo, *J. Phys. Chem.*, **69**, 2101 (1965).

[19] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, p 134.

[20] C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1963).

[21] B. N. Figgis, "Introduction to Ligand Fields," McGraw-Hill Book Co., New York, N. Y., 1966, p 306, 310.

One can calculate the spin density on the metals by squaring the t_{2g} MO's and obtaining the Mulliken overlap population.[22] The fact that reasonable spin densities (Table II) are obtained from the t_{2g} MO coefficients indicates that this calculation has properly estimated the per cent of Cl p_π bonding in the $IrCl_6^{2-}$ case. The general trend of increased ligand participation in the t_{2g} MO across the series (Table II) could be verified in the future with esr studies on the $ReCl_6^{2-}$ and $OsCl_6^{2-}$ complexes.

Nuclear Quadrupole Resonance (nqr) Coupling Constants (*eqQ*).—In nuclear quadrupole resonance one measures transitions between nuclear spin states which are split by the interaction of nuclear states with the electric field gradient produced by the electrons. Consequently, the electron distribution in well-defined atomic and molecular systems containing quadrupolar nuclei can be measured. Because the resonance frequency is dependent upon the local electronic environment of the nucleus, nqr, like esr, sometimes affords the only feasible physical method for the elucidation of electronic structure.

The interpretation of nqr spectra of halide ions has always been done in terms of a valence bond approach (the well-known Townes–Dailey treatment[23]), but for complexes in particular, and other compounds as well, a molecular orbital treatment is far more useful since it ties in directly with the general picture of electronic structures of complexes and with the results of other kinds of measurements (*e.g.*, esr, nmr) and is more flexible. A relationship between MO eigenvectors and *eqQ* values has been developed[4] and will be applied to the molecules treated in this paper.

Using eq 11 of ref 4, the nqr relationships[24] between Cl p_σ and p_π electrons, the eigenfunctions or MO coefficients,[14] and the overlap integrals,[14] we have calculated the nqr coupling constants, *eqQ*, tabulated in Table II.

The excellent agreement between calculated and observed *eqQ* values substantiates our belief that the MO method employed here gives reasonable predictions and explanations of the bonding properties in these complexes. As will be discussed elsewhere, had a free-ion degree of orbital energy dependence on charge been used, the calculated metal charge would have been much lower, the degree of M–Cl covalence much higher, and, thus, the *eqQ* values much higher than the experimental ones. Furthermore, the increase in *eqQ* across the series verifies the contention that the effective metal charge decreases across the series *via* electron donation through the Cl $3p_\sigma$ orbitals.

The occupation of the Cl orbitals is also given in Table II. Note the decrease in the number of Cl $3p_\sigma$ electrons across the series. The Cl 3s occupation stays constant, presumably because (1) the Cl 3s orbital energy is quite low with respect to that of the 3p, and (2) the Cl 3s radial wave function is less diffuse than the 3p wave function.

(22) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

(23) C. H. Townes and B. P. Dailey, *ibid.*, **17**, 782 (1949).

(24) T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1958.

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Kinetic Study on the Alkaline Hydrolysis of $Co(NH_3)_5O_2C_2Cl_3^{2+}$ and $Co(NH_3)_5O_2C_2Cl_2H^{2+}$

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The rates of hydrolysis in alkaline solution of $(NH_3)_5CoO_2C_2Cl_2H^{2+}$ and $(NH_3)_5CoO_2C_2Cl_3^{2+}$ were found to follow the general rate law $-d \ln [\text{complex}]/dt = k_1[OH^-] + k_2[OH^-]^2$. At 25° and $\mu = 1.0$ (NaCl), for the dichloroacetato complex $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are 28.9 kcal mole^{-1} and 28.8 cal mole^{-1} deg^{-1}; and $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are 20.8 kcal mole^{-1} and 0.3 cal mole^{-1} deg^{-1}. For the trichloroacetato complex $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are 23.3 kcal mole^{-1} and 12.5 kcal mole^{-1} deg^{-1}; $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$ are 22.3 kcal mole^{-1} and 8.5 cal mole^{-1} deg^{-1}. The values for k_1 verify trends predicted for an SN1CB mechanism. The results are discussed with relation to acid hydrolysis of these complexes and the hydrolysis of the organic esters.

Introduction

Although the alkaline hydrolysis of both $Co(NH_3)_5O_2C_2Cl_2H^{2+}$ and $Co(NH_3)_5O_2C_2Cl_3^{2+}$ have already been studied,[1] recent work on $Co(NH_3)_5O_2C_2F_3^{2+}$ has revealed a term in the rate law second order in hydroxide ion.[2] This path proceeds with O–C bond breaking. The present study was undertaken to determine the effect of changing the carboxylate ligand on this $k_2 \cdot [OH^-]^2$ path. The results also determine whether the formerly observed trend[1] in rates for these complexes is due to an enthalpy or entropy of activation effect.

Experimental Section

Preparation and Analysis of Complex Salts.—Both the dichloroacetato and trichloroacetato complexes were prepared by

(1) F. Basolo, J. G. Bergman, and R. G. Pearson, *J. Phys. Chem.*, **56**, 22 (1952).

(2) R. B. Jordan and H. Taube, *J. Am. Chem. Soc.*, **88**, 4406 (1966).