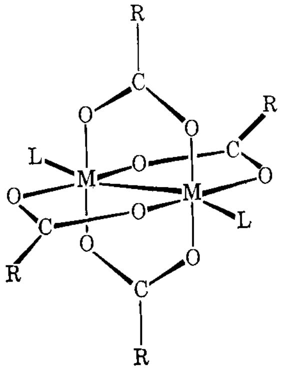

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L, may be neutral molecules or anions, or may be absent), provide circumstances well suited to the study of the strength and nature of metal-to-metal (M–M) interactions as a function of electron configuration, formal charge, and position in the periodic table. The metal atoms are relatively free to move over fairly wide limits along the fourfold axis in accord with the magnitude and sign of the interaction between them. Thus, in a variety of copper(II) complexes the Cu–Cu distances[2,3] are in the range 2.62–2.71 Å, indicative of only slight interaction. Magnetic studies[3] confirm that only weak antiferromagnetic spin couplings occur. In $Mo_2(O_2CCH_3)_4$[4] and several $Re_2(O_2CR)_4X_2$ species,[5,6] on the other hand, extremely short distances (Mo–Mo, 2.11 Å; Re–Re, 2.24 Å) imply very strong M–M interactions which can be formulated as quadruple bonds.[1,7]

Chromous acetate, $Cr_2(O_2CCH_3)_4(H_2O)_2$, has always been regarded as exhibiting very weak M–M interaction. The structure was reported[8] to be similar to that of $Cu_2(O_2CCH_3)_4(H_2O)_2$ with a Cr–Cr distance of 2.64 Å. Even though the compound is diamagnetic,[9] such a distance has been regarded[1,9,10] as too long to allow for substantial M–M bonding. Thus Figgis and Martin[9] concluded that "since the internuclear Cr–Cr distance is identical to that observed in copper acetate, the bonds (*i.e.*, σ, π and δ components of a quadruple interaction) are unlikely to be strong. This conclusion is supported by evaluation of the overlap integrals." Of course, at the distance of 2.64 Å the overlap integrals had to be very small. Similarly, Cotton[1] wrote: "Is there any more involved (in $Cr_2(O_2CCH_3)_4(H_2O)_2$) than just interionic coupling of spins? Is there actually a Cr–Cr bond? The structural parameters (*i.e.*, Cr–Cr = 2.64 Å) indicate clearly that there is no bond."

More recently, however, various considerations led us to question the reasonableness of the *seemingly* proved weakness of the Cr–Cr interaction. A critical examination of the report on the structure[8] raised grave doubts as to its reliability; the reported distance appeared to be only a rough estimate, arbitrarily equated to that reported earlier for the copper compound. A single-crystal structural study[11] has now shown that the Cr–Cr distance is 2.362 (1) Å.[12] The quadruple M–M interaction is thus a strong one and the electronic structure and spectrum of the molecule must be (and are being) reconsidered on the basis of new MO calculations. This result has far-reaching significance because it implies that strong M–M bonds may be important in the chemistry of the metals of the first transition series as well as for the heavier metals.[13]

We have also reinvestigated the structure of $Rh_2(O_2CCH_3)_4(H_2O)_2$, which was reported[19] in 1962 to have a structure of type I with a Rh–Rh distance of about 2.45 Å. This number was, apparently, an estimate based on inspection of two electron density projections. Because the nature of the M–M bond in this compound is of much importance in understanding the electronic structures of a number of structurally homologous compounds in the same region of the periodic table, accurate structure parameters were needed. A fresh crystallographic study[20] has shown that the M–M bond is significantly shorter than previously implied, namely, 2.386 (3) Å; the mean Rh–O (acetate) distance is 2.04 ± 0.01 and the Rh–OH_2 distance is 2.308 (3) Å. We believe that these dimensions are in accord with the previous proposals[7,21] of a multiple (as opposed to single) Rh–Rh bond in this compound.

Full reports on both structures as well as detailed discussions of the M–M bonds are in preparation.[22]

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(12) The mean Cr–O (acetate) is 2.02 ± 0.02 Å; the Cr–OH_2 distance is 2.284 (3) Å.

(13) Recent data[14-16] on three binuclear nickel(II) complexes also point in this direction. Also, the reports[17,18] of a very short Cr–Cr bond (1.95 Å) in $Cr_2(C_3H_5)_4$ become more credible in light of the structure reported here; the bond in that compound must be formulated as a quadruple one though the relatively low symmetry makes the picture less simple than it is for species of D_{4h} symmetry, such as $M_2X_8^{n-}$ or $M_2(O_2CR)_4L_2$.

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Reaction of Carbonyl Groups with Perchloric Acid. *gem*-Diperchlorates[1]

Sir:

Superacid media that have received wide attention in carbonium ion chemistry,[2] such as combinations of

(1) This work was supported by the Office of Naval Research.

(2) See, for example, R. J. Gillespie, *Accounts Chem. Res.*, **1**, 202

fluorosulfonic acid, sulfur dioxide, and antimony pentafluoride, are also strongly ionizing media. Perchloric acid is unusual among the very strong acids in that it has appreciable solubility in such nonpolar solvents as chlorinated hydrocarbons.[3] Since the maximum strength of an acid is limited by that of the conjugate acid of the solvent, such solutions should result in maximum acidity[4] accompanied by high nucleophilicity of the anion. The present study is concerned with reactions of carbonyl compounds with anhydrous perchloric acid in chlorinated solvents.

The addition of acetone to a 20% excess of 10% perchloric acid in chloroform resulted after several minutes in the separation of a heavy liquid. The nmr spectrum of the chloroform layer showed only a single signal other than that of chloroform, a sharp singlet at δ 2.59. Perchloric acid, which appears in chloroform at δ 8–12 (depending on concentration), was absent. The infrared spectrum showed major peaks at 9.0 and 9.2 μ and no carbonyl or hydroxyl peaks. Removal of the solvent from a similarly prepared solution gave a slightly yellow liquid which gave analytical data consistent with 2,2-diperchloratopropane. *Anal.* Calcd for $C_3H_6O_8Cl_2$: C, 14.93; H, 2.50. Found: C, 14.45; H, 2.72. The titrimetric equivalent weight of a sample quenched with ice was 126 (120.5 theoretical). The lack of acidic hydrogen signals in the nmr spectrum and of hydroxyl or carbonyl peaks in the ir spectrum rules out addition complexes and indicates that the product is the covalent diperchlorate, $(CH_3)_2C(OClO_3)_2$.

The lower layer contained a considerable amount of perchloric acid. When the reaction was carried out with a stoichiometric amount of perchloric acid using methylene chloride as the solvent, no separate layer formed but the same product was formed. The material could be distilled at 52° (0.1 mm), and the nmr spectrum of the distillate was identical with that of the chloroform solution. Differential thermal analysis showed an exotherm starting at 85° with a peak at 159°, followed by a second exotherm starting at 202° with explosion at 250°. The diperchlorate was very sensitive to moisture, and drybox handling was required for analysis. The impact sensitivity of the material could not be determined readily because of the hydrolytic instability, but inasmuch as alkyl perchlorates are generally sensitive explosives, manipulations should be carried out remotely.

The same reaction took place with 2-butanone and excess perchloric acid in chloroform, and the diperchlorate was identified by elemental analysis.

These are the first reported examples of *gem*-diperchlorates. Further work is in progress to determine the generality of the reaction.

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