Table I. Energy of the d–d Band for Low-Spin Square-Planar Ni(tetramine)$^{2+}$ Complexes, in Aqueous Solution

Ligand	ν(d–d), cm^{-1}	Ligand	ν(d–d), cm^{-1}
[12]aneN$_4$	23 260	2,2,2-tet	22 500
[14]aneN$_4$	22 470	2,3,2-tet	22 420
[15]aneN$_4$	21 510	3,2,3-tet	21 740
		3,3,3-tet	21 050

square-coplanar stereochemistry, as required in order to stabilize the singlet state of nickel(II) ion.

The impossibility of reaching 100% of the yellow species and determining its limiting spectrum prevents us from making a thermodynamic assessment of the blue-to-yellow equilibrium for [12]aneN$_4$ complexes at a fixed ionic strength. However, taking a value of 65 ± 15 for the molar extinction coefficient of Ni([12]aneN$_4$)$^{2+}$, yellow, as presumed from analogous complexes with cyclic and open tetramines,[13] it can be calculated that at 22 °C in 6 M NaClO$_4$ Ni([12]aneN$_4$)$^{2+}$ exists as 19 ± 6% in the yellow planar form, which becomes 37 ± 10% at 80 °C. On the other hand the room temperature guessed percentage of low-spin Ni([12]aneN$_4$)$^{2+}$ at lower salt concentration is 9 ± 2 (3 M NaClO$_4$), less than 1% in pure water. It must be noticed that the formation of the yellow species is much more favored with other tetramines (for instance, in 6 M NaClO$_4$, [14]aneN$_4$ and 2,3,2-tet[14] complexes exist as 100% of the yellow form; Ni(2,2,2-tet)$^{2+}$ as about 70%). The so-called "blue" species in eq 1 must be potentially considered as a mixture of cis α, cis β, and trans octahedral forms,[15] depending upon the nature of L, their quantities being regulated by equilibrium constants for the individual reactions, which makes the interpretation of the equilibrium constant for eq 1 complicated.

In any case, the existence of a square-coplanar Ni([12]-aneN$_4$)$^{2+}$ fits quite well with previous theoretical considerations on the arrangement of macrocyclic ligands around metal ions.[2] The recommended metal–nitrogen distance for [12]aneN$_4$ in its minimized strain square configuration is 1.83 Å. Low-spin nickel(II) ion in various polyamine complexes exhibits Ni–N distances of 1.90–1.91 Å[16a,17] and the reduced size of low-spin Ni(II) should allow easier fitting of the macrocyclic hole. Therefore, coplanar chelation of [12]aneN$_4$ is promoted by the small size of Ni(II) together with its strong preference for square coordination. These two properties make low-spin Ni(II) unique among the 3d metal ions. The difficulty in obtaining the yellow low-spin complex, in comparison with other cyclic and open-chain tetramines, which is expressed by the low constant for eq 1, probably reflects the large steric energy spent by [12]aneN$_4$ on changing from a cis to a trans configuration.

In Table I the energy of the visible band of Ni([12]-aneN$_4$)$^{2+}$, yellow, is compared with that of complexes of upper homologues [14]aneN$_4$ and [15]aneN$_4$ and of some complexes of open-chain tetramines. The band energy for the low-spin Ni(II) tetragonal chromophore furnishes a measure of the in-plane metal–donor interaction.[11] It is seen that *the smallest macrocycle [12]aneN$_4$ exerts the strongest perturbation* and presumably forms the most exothermic bonds, among all the ligands under consideration. Similarly, for open ligands, increasing the size of chelate rings causes a decrease of the in-plane interaction. The effect of mechanical constraints of the ligand on the metal–donor interaction energy has been predicted.[2,18] [12]aneN$_4$ is the most appropriate ligand to establish strong local interactions with the low-spin nickel(II) ion as it offers its donor atoms at the most appropriate distance and in the most favorable positions (the corners of a square).

Registry No. Ni([12]aneN$_4$)$^{2+}$, 56647-83-7; Ni([14]aneN$_4$)$^{2+}$, 46365-93-9; Ni([15]aneN$_4$)$^{2+}$, 53277-08-0; Ni(2,2,2-tet)$^{2+}$, 24653-01-8; Ni(2,3,2-tet)$^{2+}$, 25669-75-4; Ni(3,2,3-tet)$^{2+}$, 63528-06-3; Ni(3,3,3-tet)$^{2+}$, 35821-92-2.

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Istituto di Chimica Generale   **Luigi Fabbrizzi**
  e Inorganica dell'Università
  e Laboratorio CNR
50132 Florence, Italy

Existence of Direct Metal-to-Metal Bonds in Dichromium Tetracarboxylates

Sir:

Since 1964 when the existence of quadruple bonds between transition metal atoms was first recognized[1] several hundred papers dealing with these and closely related multiple bonds between metal atoms have appeared.[2] Such bonds are best known between pairs of molybdenum atoms and pairs of rhenium atoms, though Tc–Tc, W–W,[3,4] and Cr–Cr bonds of order >3 are also well characterized. With respect to chromium, the proposal of quadruple bonds in the Cr$_2$(CH$_3$)$_8^{4-}$ ion[2] (d_{CrCr} = 1.980 (5) Å) and in Cr$_2$(C$_3$H$_5$)$_4^{2}$ (d_{CrCr} = 1.97 Å) has not been disputed. Also in CrMo(O$_2$CCH$_3$)$_4^5$ (d_{CrMo} = 2.050 (1) Å) the existence of such a bond is not controversial. There has, however, been some controversy about the electronic structures of substances with the general formula Cr$_2$(O$_2$CR$_4$)·2L and the general structure **1**, which has D_{4h} symmetry.

The first such compound (R = CH$_3$; L = H$_2$O) was discovered in 1844 and a host of others have since been reported. They are all atypical of Cr^{II} compounds generally in being red and essentially diamagnetic rather than blue and paramagnetic. Only in 1970 was one of these compounds correctly characterized structurally[6] at which time it was specifically proposed that a "strong bond exists between the metal atoms", since the Cr–Cr distance was found to be 2.361 (1) Å. We have since shown[7] that in anhydrous Cr$_2$(O$_2$CCH$_3$)$_4$ the metal–metal distance is even shorter, viz., 2.288 (2) Å, al-

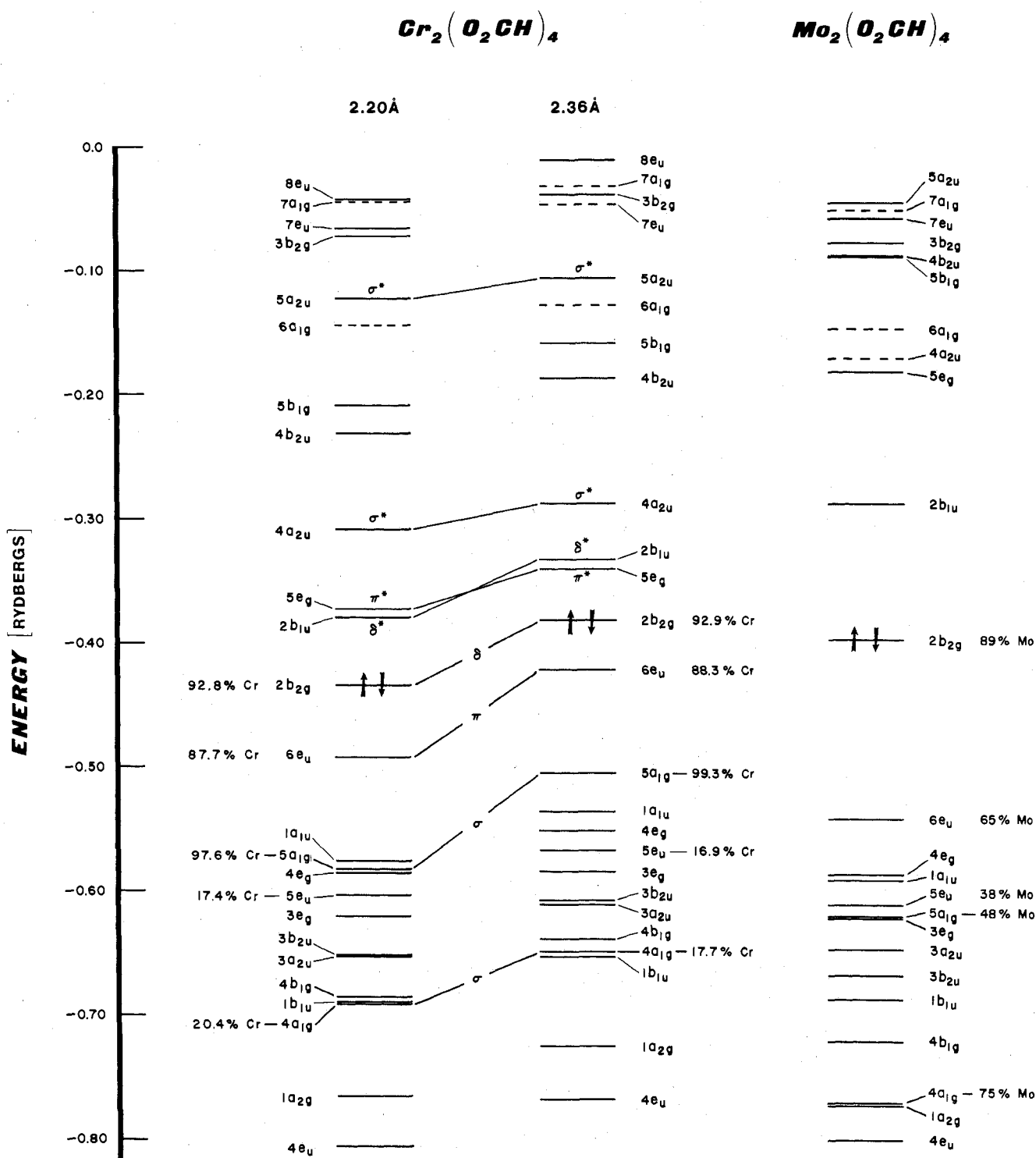$$Cr_2\left(O_2CH\right)_4 \qquad\qquad Mo_2\left(O_2CH\right)_4$$

Figure 1. SCF-Xα MO energy level diagram for $Cr_2(O_2CH)_4$ and $Mo_2(O_2CH)_4$. The highest filled molecular orbital in each case is $2b_{2g}$ and is marked as such. Dashed levels indicate diffuse Rydberg states which contain less than 20% of their charge density within the atomic spheres. Percent characters are given only for orbitals which are metal–metal bonding and have Cr contributions greater than 10%.

though in $Cr_2[O_2CC(CH_3)_3]_4$ it is 2.39 Å[8] and in $Cr_3(O_2-CH)_6(H_2O)_2$ about 2.45 Å.[9] In all these cases, there are axial ligands (L in **1**) either as separate entities or by virtue of the crystal packing which allows intermolecular sharing of oxygen atoms.[7] Such axial bonds may be expected to weaken the M–M bond[10,11] and, thus, for an isolated $Cr_2(O_2CMe)_4$ molecule a Cr–Cr distance shorter than 2.29 Å may be expected. Unfortunately, until now, the only condition under which such a molecule might have been observed is in the vapor phase and the only observation available is the photoelectron spectrum (PES).[12]

It has recently been asserted, on the basis of an ab initio calculation for $Cr_2(O_2CH)_4\cdot 2H_2O$, at a Cr–Cr distance of 2.362 (1) Å, that there is "no net bonding" between the metal atoms.[12] Such a conclusion may, in our opinion, be easily recognized as erroneous on the most elementary structural grounds. As pointed out long ago,[13] the set of four bridging carboxyl groups arranged as in **1** is a framework within which a pair of metal atoms may adopt any internuclear separation consistent with the forces directly between them. Thus, the cases of $Co_2(O_2CC_6H_5)_4\cdot 2quin$[14] where Co–Co = 2.832 (2) Å and numerous $Cu_2(O_2CR)_4\cdot 2L$ compounds[15] with Cu–Cu
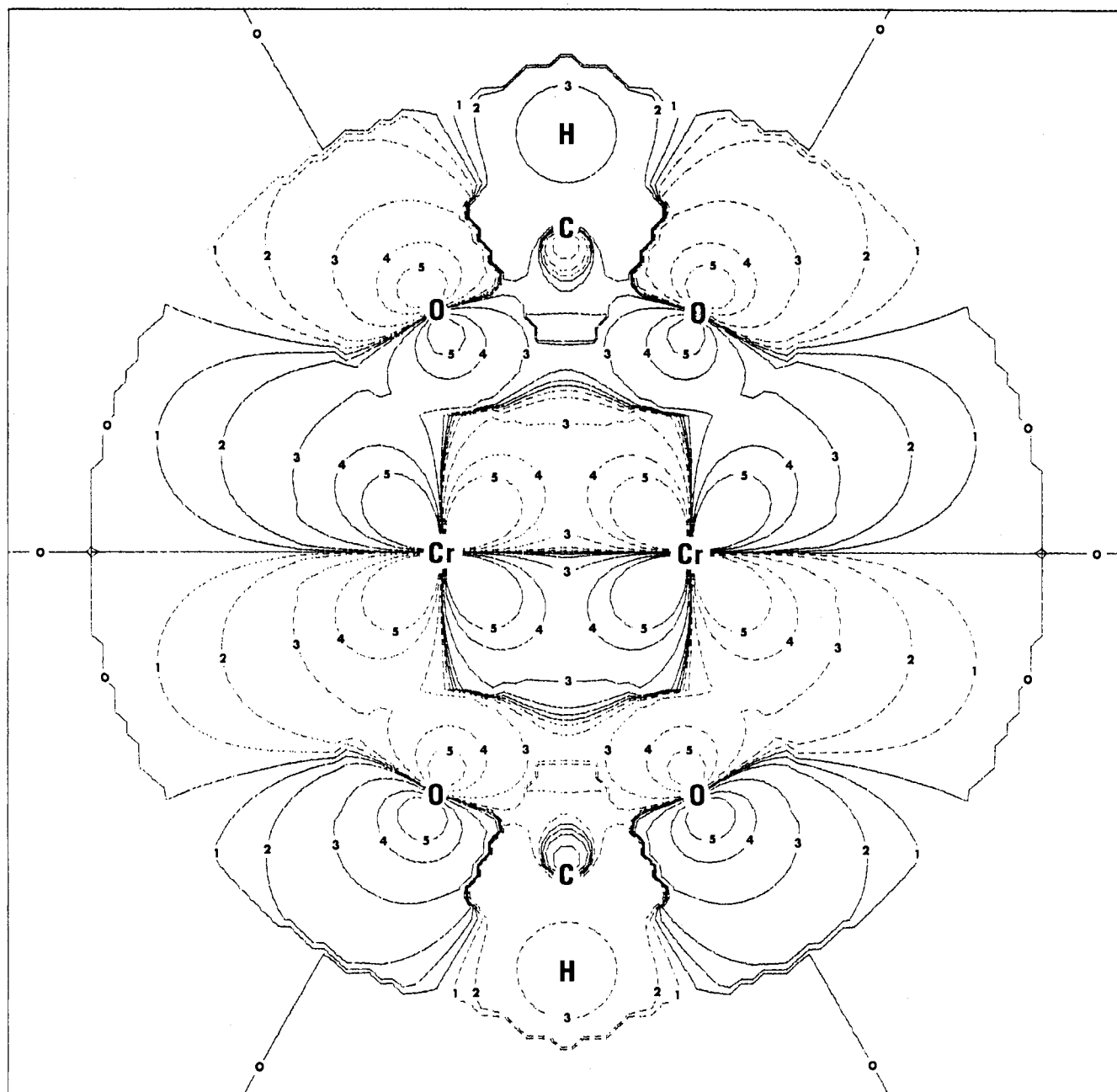
Figure 2. A contour diagram of the $6e_u$ orbital of $Cr_2(O_2CH)_4$ from the calculation for Cr–Cr = 2.20 Å. Contour values for 0, ±1, ±2, ±3, ±4, and ±5 are 0.00, 0.003, 0.008, 0.030, 0.080, and 0.130. Negative contours are denoted by dashed lines.

distances in the range 2.6–2.7 Å illustrate what may be expected if the metal atoms are not bonded significantly to each other.

Distances such as 2.36 Å (and a fortiori 2.29 Å) proclaim the existence of a Cr–Cr bond. Since the correct Cr–Cr distance in $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ was reported,[6] *the question has not been whether there is such a bond but only how best to describe it.* One of us has previously[3] observed "that quadruple bonds can vary in strength and that bond multiplicity is not a direct or single-valued index of bond strength". It was proposed[2] that $Cr_2(O_2CCH_3)_4 \cdot 2H_2O$ "contains a quadruple bond", though not a strong one. We now reiterate that claim and report briefly calculations to verify the quadruple bond.[25]

The results of SCF–Xα–SW calculations on $Cr_2(O_2CH)_4$ at Cr–Cr = 2.20 and 2.36 Å (other parameters as in crystalline $Cr_2(O_2CCH_3)_4$[7]) are shown in Figure 1 where they are compared with the results of Norman et al.[17] for $Mo_2(O_2CH)_4$.

By and large the results speak for themselves. However, we call particular attention to the different arrangements of the $4a_{1g}$ and $5a_{1g}$ orbitals in the two cases. Contour diagrams that space limitation does not allow us to present here[18] show conclusively that in the molybdenum case $4a_{1g}$ is largely Mo d_{z^2} in character and mainly Mo–Mo σ bonding while $5a_{1g}$ is less Mo–Mo bonding and is antibonding with respect to Mo–O. In $Cr_2(O_2CH)_4$, $4a_{1g}$ and $5a_{1g}$ are much closer together with their character and roles regarding M–M bonding reversed, as implied by the percentages in Figure 1. Thus the σ component of the quadruple bond is considerably weaker for Cr–Cr than for Mo–Mo. This, in turn, has the effect of weakening and hence lengthening the Cr–Cr bond as compared to what one might naively expect using conventional atom radii for Cr(II) and Mo(II), or even using more sophisticated considerations[19] of this kind. Nevertheless, one is still dealing with a *quadruple bond*. The relative importance of metal–metal and metal–ligand σ overlaps will change in going from

1
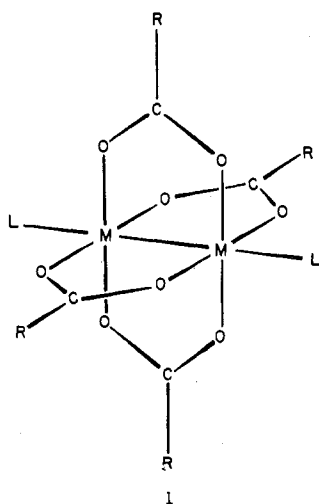
the first to the second transition series or on altering the oxidation number of the metal atoms. Because changes of this sort can significantly change the strength and hence the bond distance, *without changing the bond order*, of multiple, especially quadruple, bonds, it is *not* permissible to employ arguments in which a simple, monotonic relationship between internuclear distance and bond order is posited. As we have said before,[20] but it still appears to need emphasis, "bond multiplicity is simply a measure of the number of electron-pair interactions and not a measure of bond strength (or length)".

It is interesting to note that since the completion of this work, Benard and Veillard[21] have shown that the reason for the abject failure of the published LCAO–HF–SCF calculation[12] is, not too surprisingly, the failure of such a one-configuration calculation to take proper account of electron correlation. The usual method of taking some account of correlation within the framework of the HF–SCF approach is to introduce configuration interaction (CI), and Benard and Veillard have found that upon introducing a limited amount of CI (an expensive activity) a "completely different description of the bonding is achieved", namely, a Cr–Cr bond is found in the ground state.

In the one-configuration calculation,[12] the π-bonding (or what would have been) orbital lies at too high an energy to be occupied. Figure 2 shows one of the $6e_u$ orbitals which, according to our calculation, are the ones chiefly responsible for Cr–Cr π bonding; these orbitals *are occupied* in our picture, and as the contour diagram makes clear, they are of exactly the shape expected for an MO whose provenance, in an LCAO description, would be in pairs of overlapping $d\pi$ orbitals.

The ability of the SCF–Xα–SW calculations reported here to give straightforwardly a correct ground-state picture of the $Cr_2(O_2CH)_4$ molecule is noteworthy. It is attributed to the fact that, as Slater[22] and others[23] have pointed out, the Xα method automatically takes care of some parts of the correlation problem. It is for this reason, as is well-known, that SCF–Xα–SW calculations generally give correct dissociation products for diatomics while (single-configuration) HF calculations frequently do not.[24]

Finally, we note with satisfaction that within the limits of Koopman's theorem the patterns of calculated energy levels for $Cr_2(O_2CH)_4$ in the Cr–Cr range 2.20–2.36 Å (which we are rather confident will include the actual values in the gaseous $Cr_2(O_2CR)_4$ molecules) fit the reported[12] PES envelope very well. Thus, for the energies of the first few observed and first calculated ($2b_{2g}$) ionizations, calling the first one in each case zero, we have the following comparison, where we list observed energies followed by calculated ones in parentheses: 0 (0 for $2b_{2g}$), 0.45 (0.55 for $6e_u$), 1.55 (1.6 for $5a_{1g}$), etc. The reader may easily verify that there is semi-

quantitative agreement all the way to the $4e_u$ level of Figure 1 between the observed PES contour[12] and the calculated distribution of energy levels. We shall discuss the PES more fully when ionization energies have been calculated with allowance for relaxation.

Registry No. $Cr_2(O_2CH)_4$, 63448-51-1.

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(24) We are grateful to the National Science Foundation for partial support of this work.
(25) Cf. the Bellman's dictum: "What I tell you three times is true." Lewis Carroll, *The Hunting of the Snark, Fit the First*, Verse 2.

Department of Chemistry   **F. Albert Cotton***
Texas A&M University   **George G. Stanley**
College Station, Texas 77843

Hydrogen Halides and Hydrogen Bonds

Sir:

A previous paper[1] on the strength of the hydrohalic acids put forth the following proposals: (a) hydrogen halide molecules in aqueous solution are hydrogen bonded to the water, and therefore the standard free energy of solution of HX(g) in water should be rather negative, and (b) the standard free energy of solution for all HX should be nearly constant and the same as for HF, namely, −5.6 kcal/mol.

Pauling[2] has taken issue with the assumption of hydrogen-bond formation and has also reiterated a previous proposal[3] for estimating the ionization constants of the hydrogen halides. (His paper was overlooked in the literature search.) The present article is a more detailed examination of the available information of hydrogen bonding of hydrogen halides and its relevance to the question concerning hydrogen bonding to water.

Why a Hydrogen Bond? The intermolecular forces of attraction between molecules are generally ascribed mainly to dipole–dipole forces, dipole–induced dipole forces, and London or dispersion forces. For molecules which are free to