however, has the normal nitrile band at 2222.5 cm.$^{-1}$,[8] and no absorption at the normal C=C position similar to the data found for previously reported AN complexes of Mo[1] and Ni[2] carbonyls, in which the ligand is believed to be bonded to the metal through the C=C group (verified by X-ray diffraction for (AN)-$Fe(CO)_4$[3]).

Proton resonance lends unequivocal support to the above assignment. I shows a pattern essentially identical with the 13-line ABC type spectrum of pure AN, but generally shifted downfield by 0.5 p.p.m. This is consistent with assignment of such protons to carbon atoms not directly bonded to the metal, as, for instance, in III, where the proton singlet is seen shifted downfield 0.6 p.p.m. from that in pure acetonitrile. On the other hand, II shows a greatly perturbed proton resonance pattern, with a new singlet appearing far upfield (4.7 p.p.m.) and another one downfield (1.1 p.p.m.) from the center of the usual AN pattern, where only a few lines are now observed.

I was found to give a Diels–Alder adduct in high yield with cyclopentadiene on stirring overnight in alcohol. This product was identical with that obtained from displacement of acetonitrile with 2,2,1-bicyclo-2-heptene-6-carbonitrile. The *exo* and *endo*-cyclic isomers could be separated by thin layer chromatography. *Anal.* Calcd. for $(C_8H_9N)W(CO)_5$: C, 35.23; H, 2.05; N, 3.18. Found: C, 34.26, 33.78; H, 2.08, 1.87; N, 3.05, 3.06. The infrared nitrile frequency has been shifted from 2242 cm.$^{-1}$ in the free ligand to 2265 and 2278 cm.$^{-1}$ in the complexes, suggesting attachment *via* the nitrogen of the nitrile group. Furthermore I was recovered unchanged after treatment with 1 mole of H_2SO_4 and *t*-butyl alcohol in glacial acetic acid for 2 hr. These conditions typically cause alkylation of free nitrile groups giving N-substituted amides.[9] The absence of this typical organic reaction suggests that the nitrile group is tied up.

It is interesting to note that II shows three infrared active CO stretching absorptions (1980, 1911, and 1842 cm.$^{-1}$),[10] suggesting a *trans* structure (C_{2v}) even though it was prepared from IV, which has two CO bands, expected of an all-*cis* structure (C_{3v}).[11] The olefin group is well known, however, to have a strong *trans* effect in substitution reactions of its complexes,[12] which would apparently be above that of the carbonyl group in this case. The isomerization then would be expected to occur either during or after the substitution of three AN groups, through the directing effects of the metal-bonded C=C group.

Acknowledgment.—We are indebted to Miss Bonnie Ross for infrared interpretation, Dr. Wm. Ritchey for n.m.r. interpretation, and Mrs. Jeanette Grasselli and Dr. Herbert Kaesz (of U. C. L. A.) for very helpful discussions.

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(8) Nitrile stretching frequency for I was measured in *n*-hexane solution, and that of II in acetone solution. These bands measured in Nujol appear at 2252 and 2221 cm.$^{-1}$, respectively.

(9) H. Plaut and J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

(10) Metal carbonyl bands for II were measured in acetone, the corresponding bands appear at 1979, 1901, and 1833 cm.$^{-1}$ in Nujol.

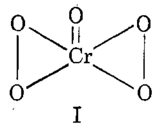
(11) R. Poilblanc and M. Bigorgne, *Compt. rend.*, **250**, 1064 (1960).

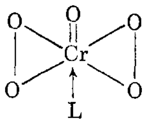
(12) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

The Structure of Perchromic Acid

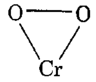
Sir:

We wish to comment on the structure (I) usually given for perchromic acid, CrO_5, and on the structures of some related compounds.


I

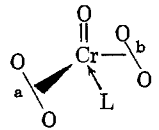

II

The first point is that I is inadequate in that this compound exists only in aqueous or non-aqueous (donor) solution, or as a solid formed with some donor molecule,[1] so that the structure always should be given as II, where L is H_2O, $(C_2H_5)_2O$, pyridine, phenanthroline, etc. The fact that the compound is highly reactive when L = H_2O does not affect this argument. Structure II contains formally six-coördinate Cr^{VI}, and although this probably is preferable to the five-coördination of I, it does not agree with the general finding that complexes of transition metals in very high oxidation states are tetrahedral. Further, and more important, both I and II require three-membered rings



with small O–Cr–O bond angles; the angle in K_3CrO_8, as found by X-ray methods,[2] is only 46°, implying considerable strain.

We believe that these difficulties can be avoided by regarding the O_2^{2-} groups as π-donors so that the Cr^{VI} is in fact tetrahedral (III), with the O_2^{2-} lying normal to the directions Cr–a and Cr–b. Donation from the filled π-orbitals of O_2^{2-} is analogous to that


III

suggested for olefin– or acetylene–transition metal complexes. Back-donation is impossible, both because of the formal absence of d-electrons on Cr^{VI}, and of the presence of filled antibonding orbitals in O_2^{2-}. However, the very high charge on the chromium should en-

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(1) D. F. Evans, *J. Chem. Soc.*, 4013 (1957).

(2) R. Stomberg and C. Brosset, *Acta Chem. Scand.*, **14**, 441 (1960).

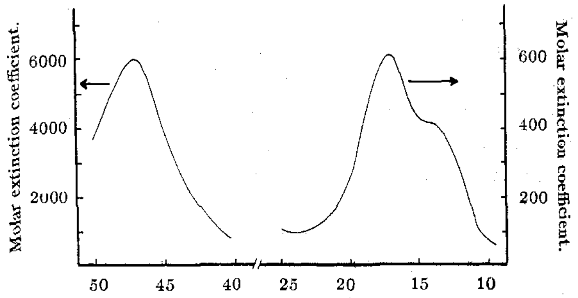

Fig. 1.—The ultraviolet and visible absorption spectrum of perchromic acid in tri-*n*-butyl phosphate solution.

sure good π-donation, in contrast to olefin compounds, in which the metal always appears in a low oxidation state.

The ultraviolet and visible absorption spectrum of CrO_5 is in agreement with the proposed structure. The spectrum (Fig. 1) of a solution of CrO_5 in tri-*n*-butyl phosphate (Cr^{VI} concentration 10^{-3} *M*) is similar to those reported by Evans,[1] the main features being a strong ($\epsilon \approx 6 \times 10^3$) band at 46.9 kK, and a doublet at 17.3 and 13.5 kK (ϵ = 610 and 410, respectively). The doublet has the energy and intensities expected of a distorted tetrahedral, rather than octrahedral, structure, in which electrons from the ligands have been donated into the d-orbitals of the chromium. The high-energy transition is probably a charge-transfer process.

It is believed that all the known properties and structure of perchromic acid, and related peroxy chromium compounds,[3] can be understood in terms of π-donor peroxy ligands. In fact, with the exception of anions in which the peroxy group acts as a bridge,[4] peroxy complexes seem to be typically formed with transitions metals in very high oxidation states, so that this type of π-donation may be of general importance.

Addendum.—Since the above communication was submitted, Stomberg [*Nature*, **196**, 570 (1962)] has published preliminary results of an X-ray structural determination of the CrO_5·pyridine adduct. His results confirm the above chemical arguments fully, in that the arrangement of CrO_5·N atoms, a distorted pentagonal pyramid, is close to that predicted by structure III above. From Stomberg's structural parameters, we find the relevant bond distances and angles in III are

Distances, Å.		Angles[a]	
Cr=O	1.72	O–Cr–N	96°
Cr–N	2.09	a–Cr–b	121°
Cr–a (=Cr–b)	1.69	a–Cr–O	112°
		a–Cr–N	109°

[a] To the nearest degree.

The essential coördination of Cr(VI) in this compound is therefore a distorted tetrahedron, and we regard this as confirming the description of the peroxy group as a π-donor. The large a–Cr–b angle suggests that one reason for the distortion from a regular tetrahedron is mutual repulsion between the negatively charged peroxy groups.

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(3) J. E. Fergusson, C. J. Wilkins, and J. F. Young, *J. Chem. Soc.*, 2136 (1962); W. P. Griffith, *ibid.*, 3948 (1962).

(4) See H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul Ltd., London, 3rd Ed., 1960, Chapter 12.

Crystal Field Theory of Halogen Cations[1]

Sir:

Arotsky and Symons[2] recently have reviewed evidence for halogen cationic species. They have applied crystal field theory to the interpretation of the visible spectra and magnetism of the solvated I^+ prepared in oleum solutions. In this note we report our crystal field calculation and correct an unfortunate error in the previous work.

The one electron matrix elements of the crystal field are defined here by the equations

$$\langle p_0 | V_{CF} | p_0 \rangle = 2\Delta$$

and

$$\langle p_{\pm 1} | V_{CF} | p_{\pm 1} \rangle = -\Delta$$

In the case at hand it is presumed that the field to a good approximation has axial symmetry and is due to a single coördinated negative group; this requires that Δ be greater than zero—the point at which the previous analysis was in error. The diagonal crystal field matrix elements for the p^4 configuration are $-\Delta$, $^3P_\pi$; 2Δ, $^3P_\sigma$; -2Δ, $^1D_\sigma$; $-\Delta$, $^1D_\pi$; $+2\Delta$, $^1D_\delta$; 0, ^1S. The only off-diagonal element connects $^1D_\sigma$ and ^1S and is $\sqrt{8}\Delta$. The resulting energy level diagram as a function of Δ is presented in Fig. 1.

In view of the observed magnetic moment of 1.5 B.M. one would expect the ground state to be a triplet. Spin-orbit coupling leads to a splitting of the $^3\Pi$ level with the $^3\Pi_2$ component lowest. The gas phase splitting of 3600 cm.$^{-1}$ indicates that only the $^3\Pi_2$ component should be populated at room temperature. However, such a ground state cannot account for the numerical value of the magnetic moment in view of the fact that the orbital moment will add to the spin moment and that coupling to excited states is inappreciable. It should also be noted that in order to account for a spin-allowed transition in the visible region we must take the value of Δ to be about 5000 cm.$^{-1}$. This value of Δ (*cf.* Fig. 1) is close to that at which the ground state becomes a singlet. Therefore, it is tempting to assume that the ground state entails a nearly equal

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(1) Supported by the Alfred P. Sloan Foundation.

(2) J. Arotsky and M. C. R. Symons, *Quart. Rev.* (London), **16**, 282 (1962).