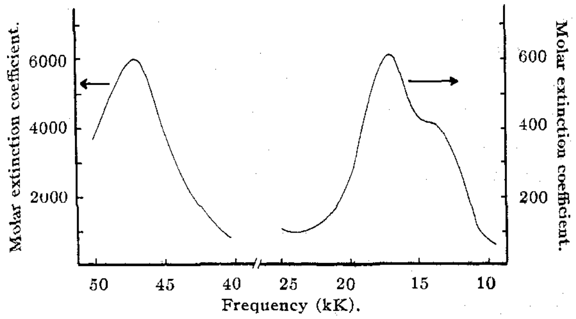

Fig. 1.—The ultraviolet and visible absorption spectrum of perchromic acid in tri-*n*-butyl phosphate solution.

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 $CrO_5 \cdot$pyridine adduct. His results confirm the above chemical arguments fully, in that the arrangement of $CrO_5 \cdot N$ 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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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

$$< p_0 | V_{CF} | p_0 > = 2\Delta$$

and

$$< p_{\pm 1} | V_{CF} | p_{\pm 1} > = -\Delta$$

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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(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.

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

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

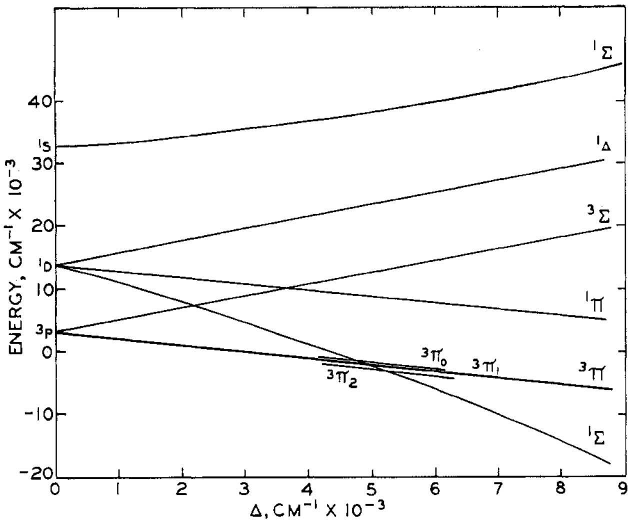

Fig. 1.—Axial crystal field splitting of the configuration p^4 The zero of energy is the free ion ground state $^3P_2$.

population of the $^3\Pi_2$ and $^1\Sigma$ states. Then the three observed transitions at 15,500, 20,000, and 24,400 cm.$^{-1}$ might be assigned to the excited states $^1\Pi$, $^3\Sigma$, and $^1\Delta$. The numerical fit is rather poor and is particularly dubious in view of the fact that the spectra then would require a ^3P–^1D term splitting of 15,500 cm.$^{-1}$, while the gas phase value is 10,650 cm.$^{-1}$; experience with transition metal ions indicates that the free ion term splittings are invariably lowered in the crystal field.

We conclude that the crystal field model does not completely account for the spectra unless the possibility of more than a single chemical species is admitted.

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On the Existence of Erbium, Thulium, and Lutetium Hexaborides

Sir:

The hexaborides of all the lanthanons (except promethium), together with some of their physical properties, have been reported.[1-4] In recent work in which relatively pure samples of the lanthanons or their compounds have been employed, one finds only isolated reports concerning the preparations of the hexaborides of erbium, thulium, and lutetium.[5-9] Furthermore, the data so far published as evidence for the preparation of these hexaborides have been minimal.

These three hexaborides were said to have been prepared by the high-temperature reaction of the lanthanon sesquioxide with boron carbide according to the equation

$$\mathrm{Ln_2O_3(s) + 3B_4C(s) \longrightarrow 2LnB_6(s) + 3CO(g)}$$

Earlier attempts by one of the authors to prepare erbium hexaboride had been unsuccessful and, as a result of these reports, efforts to prepare hexaborides of erbium, thulium, and lutetium in this Laboratory were intensified.

The respective sesquioxides were mixed with boron carbide in the molar ratio of 1:3, formed into pellets under a pressure greater than 3000 p.s.i., and then placed into a thoroughly out-gassed zirconium diboride crucible. The crucible was heated *in vacuo* to temperatures between 1100 and 1600°. The progress of the individual reactions was followed by quenching and observing the phases present after increasingly high temperatures had been attained. It was observed that the lanthanon boride phases grew in until finally no more carbon monoxide was produced and the sesquioxide phases had disappeared entirely. Invariably the predominant phase in the products of the complete reactions was the tetraboride, but, in addition, the face-centered cubic phase of the dodecaboride of the respective metal also was observed.

To assure that the presence of carbon was not affecting our results, similar reactions between the sesquioxides and elemental boron and the reactions of the metals with boron by the technique of arc-melting under an inert atmosphere were induced and resulted in the same two boride phases. Likewise, reactions conducted in a boron nitride crucible together with the arc-melting experiments demonstrated that our results were independent of the zirconium diboride crucible.

X-Ray diffraction methods were used to detect and identify the phases in the reaction products. In no case was even a trace of a cubic hexaboride phase detected. The d-values from a typical X-ray powder photograph are listed in Table I.

For a cubic hexaboride of erbium having $a_0 = 4.10$ Å., the three most intense reflections would have calculated d-values of 4.10, 2.90, and 2.37 Å. (hkl = 100, 110, and 111, respectively).

La Placa, Binder, and Post[10] report that the stability of the dodecaborides of dysprosium, holmium, erbium, thulium, lutetium, and yttrium appears to be a function of the effective size of the metal atom; they were unable to prepare dodecaborides of those metals having atomic sizes larger than dysprosium or smaller than zirconium. This strongly suggests that a similar

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[1] B. Post, D. Moskowitz, and F. W. Glaser, *J. Am. Chem. Soc.*, **78**, 1800 (1956).

[2] E. J. Felten, I. Binder, and B. Post, *ibid.*, **80**, 3479 (1958).

[3] G. V. Samsonov, *Usp. Khim.* **28**, 189 (1959); translated by F. Hilton, U.K.A.E.A. Research Group, Harwell AERE-Trans 849.

[4] H. A. Eick and P. W. Gilles, *J. Am. Chem. Soc.*, **81**, 5030 (1959).

[5] V. S. Neshpor and G. V. Samsonov, *Dopovidi Akad. Nauk Ukr. RSR*, 478 (1957).

[6] V. S. Neshpor and G. V. Samsonov, *Zh. Fiz. Khim.*, **32**, 1328 (1958).

[7] G. V. Samsonov, Yu. B. Paderno, and T. I. Serebryakova, *Kristallografiya*, **4**, 542 (1959).

[8] N. N. Tvorogov, *Russ. J. Inorg. Chem.*, **4**, 890 (1959).

[9] Yu. B. Paderno and G. V. Samsonov, *Zh. Strukt. Khim.*, **2**, 213 (1961).

[10] S. La Placa, I. Binder, and B. Post, *J. Inorg. Nucl. Chem.*, **18**, 113 (1960).