where $E_{\parallel}$ and $E_{\perp}$ are the $^2B_1 \rightarrow {}^2B_2$ and $^2B_1 \rightarrow {}^2E$ positive hole transitions, respectively; ζ is the one-electron spin–orbit coupling parameter and κ is the orbital reduction factor. $K_{\parallel}$ and $K_{\perp}$ are the principal molecular susceptibilities parallel and perpendicular to the symmetry axis of the molecule.

As indicated above, there have been conflicting interpretations of the ordering and separation of the $^2B_2$ (hole in d_{xy}) and ^2E (hole in d_{xz}, d_{yz}) states, as inferred from the electron spin resonance studies. For instance, the relative ordering of these two states as deduced recently by Harrison and Assour[12] ($^2B_2$ being above the ^2E) is at variance with the earlier calculation of Kivelson and Nieman[10] and also, to some extent, with that deduced by Gibson, *et al.*[9] However, Gibson, *et al.*, placed these two states very close together, and their calculation was somewhat uncertain because of their failure to observe the ^{14}N superhyperfine structure which was observed by all later workers. Further, the magnitudes of $E_{\parallel}$ and $E_{\perp}$ deduced by various workers differ very widely among themselves. Roberts and Koski[11] have even taken the π–π optical transitions of the organic ring as being the d–d transitions.

In Figure 1, we have plotted two theoretical curves with different $E_{\parallel}$ and $E_{\perp}$, taking $\zeta = 500$ cm^{-1} and $\kappa^2 = 0.7$. The solid curve has been drawn assuming $E_{\parallel} = 27{,}000$ cm^{-1} and $E_{\perp} = 17{,}000$ cm^{-1} which are very close to the values deduced by Harrison and Assour. The dashed curve has been drawn taking the values of $E_{\parallel}$ and $E_{\perp}$ deduced by Kivelson and Nieman (17,000 and 25,000 cm^{-1}, respectively). The close agreement of our experimental results with the solid curve confirms the ordering of $^2B_2$ and ^2E states as deduced by Harrison and Assour (*i.e.*, as shown in Figure 2). The values of ζ and κ assumed in the present calculation are in good agreement with the degree of covalency deduced from the observed ^{14}N superhyperfine structure in this compound. For no reasonable values of ζ and κ can our experimental data be fitted to the energy separations used by Kivelson and Nieman.

This result illustrates the usefulness of the paramagnetic anisotropy in deducing the electronic structure of square-planar copper compounds. Unfortunately, neither magnetic anisotropy nor electron spin resonance can be used to locate the relative position of the $^2A_1$ state beyond confirming that it lies higher in energy than $^2B_1$.

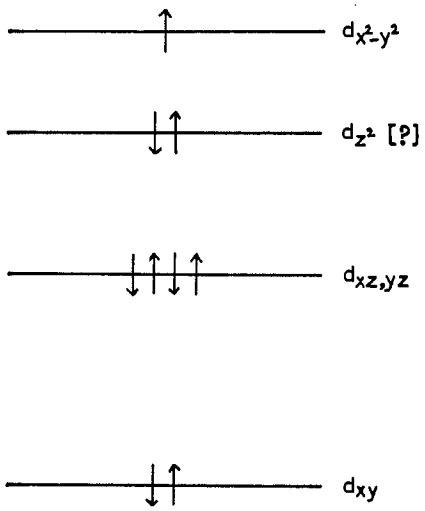

Figure 2.—A schematic representation of the electronic structure of β-copper(II) phthalocyanine.

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Electronic Structure of CrO_4^{3-} in $Ca_2(CrO_4,PO_4)Cl$

BY C. SIMO,[1] E. BANKS, AND S. L. HOLT[2]

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In the past 10 years there has been a rapidly increasing application of Wolfsberg–Helmholz type of molecular orbital calculations to the problem of electronic structure of transition metal ions.[3-5] It is interesting to note, however, that while this method is widely used, the original system to which this method was applied, namely, MnO_4^-, has yet to have its electronic structure satisfactorily described.[6-10] Indeed no small part of this problem has been the fact that until recently[11] all calculations pertaining to the MnO_4^- ion were based on inadequate data.

The study of CrO_4^{3-} was undertaken as part of a program to provide a sound experimental basis for calculations pertaining to the electronic structure of higher oxidation states.

Banks, Greenblatt, and McGarvey[12] reported the esr spectra of CrO_4^{3-}-doped single crystals of Ca_2PO_4Cl and showed that the unpaired electron is in an orbital having largely d_{z^2} character. They also reported some unpolarized absorption spectra at liquid nitrogen temperature showing bands at 37,250, 27,940, 24,500, and 17,400 cm^{-1}. These were compared to the results of Carrington, *et al.*,[13] on MnO_4^{2-} and CrO_4^{3-} and were shown to be similar. Extended optical measurement, however, produced important new features[14] which

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we report in detail. We have also included a comparison of the results of molecular orbital approximations involving transition metal ions in high oxidation states with our experimental observations. A description and critical appraisal of these theories can be found in a recent comprehensive review.[15]

Experimental Section

Solid phases with the spodiosite structure, of composition Ca_2XO_4Y, where $X^{5+} = Cr^{5+}$ or P^{5+} and $Y^- = OH^-$, Cl^-, or Br^-, were first synthesized by Banks and Jaunarajs.[16] Single crystals of the chlorospodiosites were grown from excess $CaCl_2$ flux. Better crystals of Ca_2PO_4Cl, Ca_2CrO_4Cl, and their solid solutions were grown in the same manner by Banks, Greenblatt, and Post,[17] who reported the crystal structures of the two end members of the solid solution series. The method of crystal growth was described in some detail by Kingsley, *et al.*,[18] who described and interpreted the absorption and fluorescence spectra of MnO_4^{3-}-doped Ca_2PO_4Cl.

Ca_2PO_4Cl and Ca_2CrO_4Cl possess orthorhombic crystal symmetry with four XO_4^{3-} ions per unit cell.[17] Each X atom is at the center of a tetrahedron which is distorted in such a way as to have as its only symmetry element a twofold rotation axis perpendicular to the (100) crystal face. Angular distortions are such that the geometry of the molecule closely approximates D_{2d} symmetry, however.

Optical measurements and crystal face identification were made as reported in earlier publications from this laboratory.[19-22]

Results

The complete polarized spectrum of $Ca_2[PO_4,CrO_4]Cl$, recorded at 80°K, is shown in Figure 1. Figure 2 shows the lowest energy band, recorded at liquid

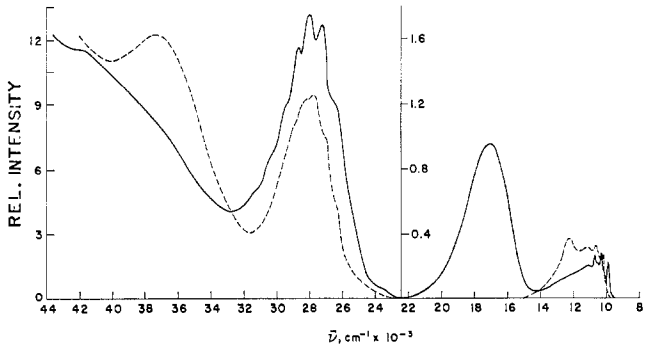

Figure 1.—The polarized spectrum of CrO_4^{3-} at 80°K.

helium temperature. The two most prominent features associated with this absorption manifold are the strongly polarized sharp lines on the low-energy end of the band and the less completely polarized manifold on the high-energy side of the band. These features are not apparent in the room-temperature spectrum but are exhibited in some detail at 80°K. The line spectra consist of four readily discernible components in the $\|a$ ($\|z$) polarization and five components in the

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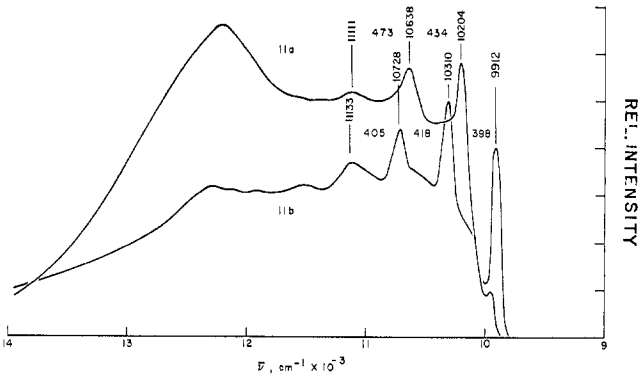

Figure 2.—The near-infrared spectrum of CrO_4^{3-} at 5°K. [The symbol $\|a$ indicates that the electric vector of the incident radiation is parallel to the a crystallographic axix ($\|z$ molecular axis); $\|b = \perp z$.]

$\|b$ ($\perp z$) polarization. These lines are obviously associated with simultaneous electronic and vibrational excitations. Positions and spacing of these lines are given in Table I.

TABLE I
LINE ABSORPTION ON 10,000–14,000-CM^{-1} MANIFOLD

$\|a$		$\|b$	
$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
		9,912	
			398
10,204		10,310	
	434		418
10,638		10,728	
	473		405
11,111		11,133	

The 15,000–21,000-cm^{-1} manifold is devoid of fine structure. Indeed, it consists of a completely polarized broad band centered at ~17,100 cm^{-1} with a weak shoulder on the low-energy side at ~15,400 cm^{-1}.

Figure 3 displays the 24,000–31,000-cm^{-1} region of

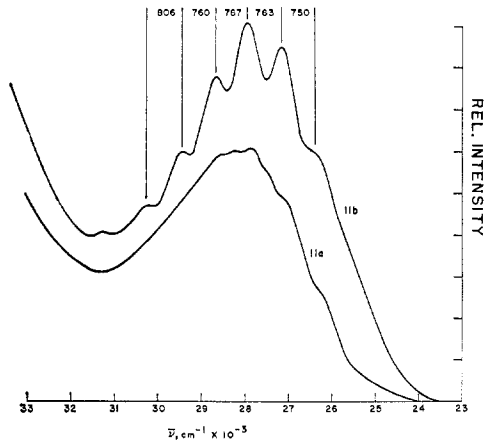

Figure 3.—The visible spectrum of CrO_4^{3-} at 5°K.

the absorption. The well-defined vibrational structure exhibited by the $\|b$ polarization is tabulated in Table II.

TABLE II
VIBRATIONAL COMPONENTS IN THE 24,000–31,000-CM^{-1} REGION OF THE SPECTRUM OF $Ca_2[PO_4,CrO_4]Cl$

‖b		‖b	
$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
26,420		28,690	
	750		760
27,170		29,450	
	763		806
27,933		30,256	
	767		

Discussion

Band Assignment.—Of the four major absorption bands which occur between 8000 and 44,000 cm^{-1}, three can be unequivocally assigned in D_{2d} symmetry (Table III, Figure 4). These assignments were arrived

TABLE III

Transition energy, cm^{-1}	Allowed	Assignment in D_{2d} symmetry
9,912	$\perp z$	$^2A_1 \rightarrow {}^2E$
10,204	$\parallel z$	$^2A_1 \rightarrow {}^2B_2$
17,000	$\perp z$	$^2A_1 \rightarrow {}^2E$
26,420	$\perp z$	$^2A_1 \rightarrow {}^2E$
26,000	$\parallel z$	$^2A_1 \rightarrow {}^2E_2$

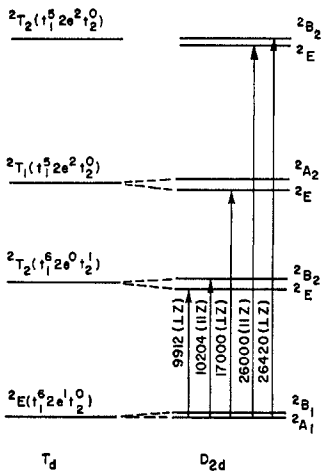

Figure 4.—The energy level diagram for CrO_4^{3-}.

at in the following way. In the ground state the single unpaired electron has been shown to occupy a d_{z^2} orbital.[12] This orbital transforms as A_1 in D_{2d} symmetry. Further, in D_{2d} symmetry, transitions $A_1 \rightarrow E$ are allowed perpendicular to the z molecular axis while $A_1 \rightarrow B_2$ transitions are allowed parallel to the z molecular axis. $A_1 \rightarrow A_2$ excitations are forbidden in both polarizations. Most current molecular orbital treatments put the ordering of the one-electron levels of interest as $t_1^6 < e^1 < t_2$ (in T_d symmetry). The lowest energy bands should thus arise from low-symmetry components of transitions associated with, in T_d symmetry, the configuration $t_1^6e^0t_2^1$ or $t_1^5e^2t_2^0$. The latter possibility can be ruled out in the following way. The configuration $t_1^5e^2t_2^0$ should give rise, in tetrahedral symmetry, to $^2T_2$ and $^2T_1$, as well as quartet states while the configuration $t_1^5e^0t_2^1$ has only a $^2T_2$ state associated with it. In D_{2d} symmetry a $^2T_2$ state splits into a $^2B_2$ and a ^2E while a $^2T_1$ state gives rise to a $^2A_2$ and a ^2E; *cf.* Figure 4. Based on the aforementioned slection rules and the fact that the low-symmetry splitting does not appear to be large (Figures 1 and 2), the band which occurs $\perp z$ at ~17,000 cm^{-1} must be the allowed $^2A_1 \rightarrow {}^2E$ component of the $^2E \rightarrow {}^2T_1$ transition, while the manifolds at ~10,000 and ~26,000 cm^{-1} must be associated with low-symmetry components of the $^2E \rightarrow {}^2T_2$ transitions arising from the $t_1^62e^1t_2^0 \rightarrow t_1^62e^0t_2^1$ and $t_1^62e^1t_2^0 \rightarrow t_1^52e^2t_2^0$ excitations. [We exclude the possibility that the 10,000-cm^{-1} manifold might arise from a spin doublet to spin quartet transition on the following bases: (1) the relative intensity, compared to that of the 17,000-cm^{-1} band, is not low enough, (2) this would leave a spin-allowed transition unaccounted for, (3) no other spin-forbidden bands are observed although the $t_1^52e^2t_2^0$ configuration gives rise to more than one quartet state, (4) the intensities of the xy and the z components of a spin-forbidden transition would most likely be very different due to the ΔE term of the equation $f_{4,6} = f^0(a\zeta_{nl}/\Delta E)^2$, which governs the oscillator strength of spin-forbidden transitions.[23]] We then choose the absorption maxima at ~10,000 cm^{-1} to be associated with the d–d transition $t_1^62e^1t_2^0 \rightarrow t_1^62e^0t_2^1$ on the basis that the intensity of a transition which involves states of significant d character should be weaker than a metal to ligand, ligand to metal, or ligand to ligand transition. These assignments are consistent with a crystal field splitting energy of ~10,000 cm^{-1} rather than the value of ~17,000 cm^{-1} which has been suggested before.[6] This discrepancy must raise serious questions about the ability of some current molecular orbital approaches to predict the crystal field splitting energies even of simple molecules.

Vibrational Assignment.—On the lowest energy manifold, vibrational origins can be clearly discerned at 9912 ($\parallel b$) and 10,204 cm^{-1} ($\parallel a$). (In the $\parallel a$ polarization the weak line at ~9950 cm^{-1} is thought to be the incompletely polarized 9912-cm^{-1} absorption.) Both progressions are separated by frequencies of greater than 400 cm^{-1}; *i.e.*: $a \simeq 450$; $b, \simeq 406$ cm^{-1}. Although a fundamental of $T_2(\nu_4)$ symmetry occurring at 410 cm^{-1} has been reported for CrO_4^{3-} in Ca_2CrO_4Cl,[12] it seems unlikely that it is this vibration which is associated with both the progressions observed on the ~10,000-cm^{-1} manifold. For the 450-cm^{-1} frequency, observed in the visible spectrum, to be ascribed to this fundamental would require that the molecule be contracted in the excited state. This in turn could only occur if the transition in question was associated with an electron transfer from a nonbonding or antibonding orbital to a bonding orbital. This is clearly an impossibility no matter what assignment one gives to the 10,000-cm^{-1} band. For the progression characterized by a 406-cm^{-1} spacing, it is possible that this frequency represents a component of this $T_2(\nu_4)$ fundamental. The frequency reduction in the excited state would then perhaps be rather small. A small change in the

(23) See S. Holt and R. Dingle, *Acta Chem. Scand.*, **22**, 1091 (1968), and J. Milstein and S. L. Holt, *Inorg. Chem.*, **8**, 1021 (1969).

excited-state internuclear distance is supported by the intensity pattern of the $\|b$ vibrational progression. This would in turn tend to indicate that what would be the antibonding t_2 orbital in T_d symmetry is not so strongly antibonding in character in D_{2d} symmetry.[24] In the $\|a$ polarization it is likely that the exciting mode is a combination of the $T_2(\nu_4)$ and a lattice vibration. Such a mode is observed at $\sim$500 cm^{-1} in the infrared spectrum of Ca_2CrO_4Cl.[25]

The analysis of the $\sim$28,000-cm^{-1} manifold is much more clear-cut and undoubtedly is associated with one of the components of the $T_2(\nu_3)$ fundamental which occur at 865, 810, and 760 cm^{-1} in the ground state.

Electronic Structure.—Various approximate molecular orbital calculations yield, at best, a reasonable ground-state, "one-electron" energy level diagram. Attempts to assign electronic spectral bands on the basis of these in any case other than d^0 ignores the excited-state electron–electron interactions and have led to a variety of speculations in the d^1 and d^2 cases.[3,6,7,13,18,26] This has, of course, been recognized[4] and some attempt is being made to include a correction for repulsion.[27] One of the more recent and successful efforts has been that of Dahl and Johansen.[10] Their calculations suggest that the correct value of $\Delta\nu$ for MnO_4^- is of the order of 10,000 cm^{-1} and not 26,000 cm^{-1} as has been previously supposed.[6] This value agrees closely with our results on CrO_4^{3-},[14] MnO_4^{3-},[21] and MnO_4^{2-} [28] and prompts us to disregard both our previous tentative assignment made for MnO_4^- and assignments made by others for the MO_4^{n-} system. Indeed, it is perhaps pertinent here to comment upon the crystal field splitting for various MO_4^{n-} ions.

As noted earlier most current interpretations of the absorption spectra of MO_4^{n-}, where n = 1–3, have indicated that Δ is a sharply increasing function of formal oxidation state.[6,11] This is clearly seen in the data presented in the center column of Table IV.

Our experimental work, however, belies the validity of the Δ values reported for the d^1 systems CrO_4^{3-} [14] and MnO_4^{2-},[28] while the Dahl and Johansen interpretation of the spectra of MnO_4^- must be considered to be the correct one.

The newer values of Δ which arise from these current efforts are shown in the last column in Table IV along with Δ values for a number of other manganese tetrahedral oxyanions.

It will be noted that the values in the right-hand side of Table IV do *not* reflect a large increase in Δ with formal oxidation state. Based upon the older values of Δ and making the reasonable assumption that changes in effective oxidation state should be reflected by similar variations in Δ, we should conclude that the effective oxidation state of Mn(VII) in MnO_4^- is much larger than that of Mn(VI) in MnO_4^{2-} which is in turn much larger than that of Mn(V), etc. This is clearly not true if one considers the newer values of $\Delta\nu$. Here, one finds that $\Delta\nu$ has reached a plateau by the time that the formal charge on the manganese ion has become +5. (This contention derives added support from the reported values of Δ for CrO_4^{3-} and CrO_4^{2-}.) From this we must conclude that the *effective charge upon the manganese ion does not increase beyond that found for Mn(V)*.

TABLE IV

Complex	Metal formal charge	Δ,[a] cm^{-1}	Δ, cm^{-1}
CrO_4^{3-}	5	16,000	10,000[b]
CrO_4^{2-}	6		$\sim$9,000[c]
MnO_4^{6-}	2		4,500[d]
MnO_4^{5-}	3		7,000[e]
MnO_4^{4-}	4		10,000[f]
MnO_4^{3-}	5	11,000	11,000[g]
MnO_4^{2-}	6	19,000	$\sim$10,000[f]
MnO_4^-	7	26,000	$\sim$10,000[c]

[a] Reference 6. [b] Reference 14. [c] Reference 10. [d] Estimated from the values given for MnO_6^{10-} and MnF_6^{2-} by C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, London, 1962, p 110. [e] Estimated from work of R. Dingle, *Acta Chem. Scand.*, **20**, 33 (1966). [f] Reference 27. [g] References 2, 18, 21.

Acknowledgment.—This work was supported by NSF Grant GP7920.

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CONTRIBUTION FROM THE INSTITUTE OF INORGANIC AND ANALYTICAL CHEMISTRY, L. EÖTVÖS UNIVERSITY, BUDAPEST, HUNGARY

Application of Diffusion Constant Measurement to the Determination of the Rate Constant of Electron-Exchange Reactions

BY I. RUFF AND I. KORÖSI-ÓDOR

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Recently a new method was suggested by I. R. for the determination of the rate constant of very fast electron-exchange reactions,[1] based on Dahms' prediction[2] of the existence of electronic conduction in aqueous solutions. Electronic conduction takes place, when there is a concentration gradient in the solution containing particles of both oxidation states of an oxidation–reduction couple and the gradient of one of them differs from that of the other in every point of the system. For the sake of simplicity, let the system consist of two parts at the time $t = 0$ which are divided by an imaginary plane at the linear coordinate perpendicular to this plane $x = 0$. Let the concentration of the species be $c_{red} = 0$ and $c_{ox} = c_0$, if $x < 0$, and $c_{ox} = 0$

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