$[H^+]$ (with $\Sigma[ClO_4^-] = 2.0$ *M*) should reveal the presence or absence of such a path.

Table I. Kinetics of the Chromium(II)-Catalyzed Aquation of CrI^{2+} (25°, $\Sigma[ClO_4^-] = 1.0$ *M*)[a]

$[H^+]$, *M*[b]	$[Cr^{2+}]$, *M*[c]	10^2k_3, sec^{-1} [d]
0.0483	0.0209	2.2
0.0715	0.0452	2.2
0.102	0.0314	2.0[e,f]
0.125	0.0452	2.2
0.125	0.0574	2.1[f]
0.130	0.0498	2.5
0.131	0.0502	2.1[e]
0.194	0.0209	2.4
0.194	0.0896	2.5[f]
0.194	0.117	2.0
0.194	0.200	2.2
0.197	0.0896	2.1[e,f]
0.500	0.123	2.1
0.502	0.0896	2.6[e,f]
		Av 2.2
0.0715	0.0452	0.86[g]
0.194	0.200	0.83[g]
0.500	0.162	0.84[g]

[a] Measurements at 475 mμ with CrI^{2+} ($3.5\text{–}5.0 \times 10^{-3}$ *M*) prepared *in situ* by the reaction of iodine with excess chromium(II), except where noted. $\Sigma[ClO_4^-]$ maintained with $NaClO_4$. [b] Calculated from the $HClO_4$ added and the $HClO_4$ in the Cr(II) solution after allowing for the H^+ consumed in the $IO_3^-\text{–}I^-$ reaction, except for measurements with purified CrI^{2+}. [c] Calculated as the difference between Cr(II) added and Cr(II) consumed in the reaction with I_2, except for measurements with purified CrI^{2+}. [d] Defined by the rate law $k_3[CrI^{2+}][Cr^{2+}]/[H^+]$. [e] Measurements at 306 mμ with $[CrI^{2+}] = 0.8\text{–}1.2 \times 10^{-4}$ *M*. [f] CrI^{2+} purified by ion exchange. [g] Measurements at 15°.

The order of reactivity for the chromium(II)-catalyzed aquations of halogenopentaaquochromium(III) complexes is I^- ($k_3 = 2.2 \times 10^{-2}$ sec^{-1}) > Br^- ($k_3 \sim 2 \times 10^{-3}$ sec^{-1}) > Cl^- ($k_3 \sim 4 \times 10^{-4}$ sec^{-1}). Undoubtedly, these reactions involve electron transfer from Cr(II) to Cr(III) by paths that do *not* make use of halide-bridged transition states. Therefore, it is noteworthy that the same order of reactivity applies to the spontaneous aquations of CrX^{2+} (for both $[H^+]$-dependent and $[H^+]$-independent paths[11]) and to the $CrX^{2+}\text{–}Cr^{2+}$ exchange reactions that proceed *via* a halide-bridged transition state.[8] This correlation suggests that the same factors may be important in determining the order of the ligands in the three classes of reactions.

It is appropriate to compare the results for the $CrI^{2+}\text{–}Cr^{2+}$ system with those for the related studies with $CrNH_3^{3+}\text{–}Cr^{2+}$ [16] and $FeCl^{2+}\text{–}Fe^{2+}$.[17] The chromium(II)-catalyzed aquations of CrI^{2+} and $CrNH_3^{3+}$ [16] proceed predominantly *via* inverse acid paths, whereas only an acid-independent path was detected in the iron(II)-catalyzed aquation of $FeCl^{2+}$.[17,18] Moreover, the appreciable difference in rates between CrI^{2+} ($k_3 = 2.2 \times 10^{-2}$ sec^{-1}) and $CrNH_3^{3+}$ ($k_3 = 5.92 \times 10^{-5}$ sec^{-1} [16]) suggests that substantial nonbridging ligand effects[6,19] are operative in these electron-transfer reactions.

Additional studies with CrI^{2+}, $CrBr^{2+}$, and $CrCl^{2+}$ as well as with other acidopentaaquochromium(III) complexes, and a discussion of the mechanism of these chromium(II)-catalyzed aquations, will be reported elsewhere.

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[16] J. H. Espenson and D. W. Carlyle, *Inorg. Chem.*, **5**, 586 (1966).

[17] R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).

[18] However, the studies with $FeCl^{2+}$ were carried out at high $[H^+]$ (1.50 to 2.85 *M*), and perhaps studies at lower $[H^+]$ might reveal a possible contribution of an inverse acid path.

[19] P. Benson and A. Haim, *ibid.*, **87**, 3826 (1965).

[20] (a) Fellow of the Alfred P. Sloan Foundation. (b) Department of Chemistry, State University of New York, Stony Brook, N. Y. 11790.

David E. Pennington, Albert Haim[20]
Department of Chemistry, The Pennsylvania State University
University Park, Pennsylvania 16802

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The Electronic Structures of Bis(β-ketoenolato)copper(II) Complexes

Sir:

The bis(β-ketoenolato)copper(II) complexes, as typified by the acetylacetonate, $Cu(acac)_2$, merit special interest because they occupy a pivotal position at the intersection of two important classes of complexes, namely, square complexes and β-ketoenolato complexes, both of which have been extensively studied in recent years.[1] Indeed the intimately related subjects of the order of "d" orbitals and the esr, the visible, and the ultraviolet spectra of the one compound $Cu(acac)_2$ have been the subject of a considerable number of publications.[2–12] However, despite these extensive efforts, the picture has remained obscure in several fundamental respects. Among the chief reasons for this are the unfortunate facts that the visible ("d–d") spectrum of $Cu(AcAc)_2$ is not well resolved in isotropic media[2] and the alignment of the molecules in the crystalline compound is such as to thwart the effort to obtain complete polarization information.[6]

In view of these circumstances we undertook the study of a closely related complex, $Cu(DPM)_2$,[13] in which the substituents on the chelate rings are *t*-butyl groups instead of methyl groups. The choice of this compound was dictated by three considerations: (1) its electronic structure should not differ in any essential way from its frustrating prototype, $Cu(acac)_2$; (2) its solution spectra show relatively good resolution and its crystal structure[14] is such that the molecules have an orientation which is exceptionally favorable for the measurement of polarizations; (3) the diamagnetic compound $Ni(DPM)_2$ is isomorphous[14] and thus

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[1] *Cf.* J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966), for a general review of β-ketoenolato complexes.

[2] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

[3] R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5668 (1958).

[4] J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961).

[5] T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

[6] J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **37**, 1569 (1962).

[7] R. H. Gersmann and J. D. Swalen, *ibid.*, **36**, 3221 (1962).

[8] C. Dijkgraaf, *ibid.*, **3**, 38 (1965).

[9] J. Ferguson, *Theoret. Chim. Acta*, **3**, 287 (1965).

[10] R. L. Belford and G. G. Belford, *ibid.*, **3**, 467 (1965).

[11] J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

[12] J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **2**, 102 (1963).

[13] DPM is an abbreviation for the enol anion of 2,2,6,6-tetramethyl-3,5-heptanedione, for which the common name is dipivaloylmethane.

[14] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).

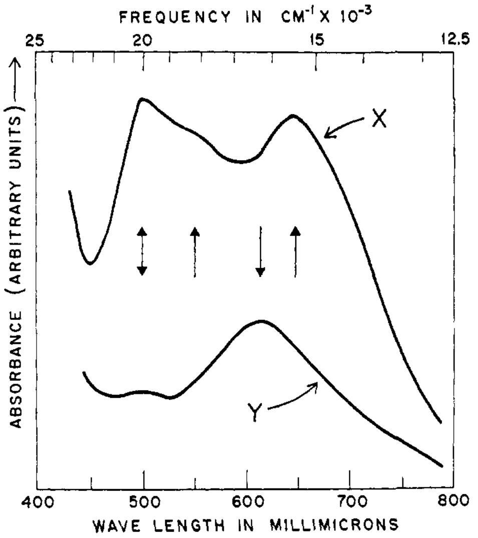

Figure 1. Spectra polarized along the x and y molecular axes for $Cu(DPM)_2$.

available as a suitable host for studies of the esr spectra of magnetically dilute $Cu(DPM)_2$. The investigation involved four phases:[15] (1) an LCAO-MO calculation[16] using the extended Hückel method and the Wolfsberg-Helmholz approximation, but with constraints imposed by the requirement that the coefficients of the d orbitals in the MO eigenvectors remain closely consistent with the magnitudes indicated for them by esr data; (2) a single crystal esr study to obtain accurate g values; (3) a study of the energies and polarizations of the visible "d-d" absorption bands; (4) a study of the near-ultraviolet (200–400 mμ) spectra and a partial reinterpretation[11,12] thereof, guided by the results of the MO calculations.

The MO calculation led to the general result, which did not change over considerable variations of the disposable parameters (*e.g.*, the Wolfsberg-Helmholz factor, the energies of Cu and O atomic orbitals) within reasonable ranges, that the d_{xy} orbital[17] lies some 18,000 cm^{-1} higher than the other four d orbitals, all of which lie within a few thousand wavenumbers of one another. This would suggest that the incompletely resolved absorptions observed for $Cu(DPM)_2$ and $Cu(acac)_2$ in the region 15,000–20,000 cm^{-1} include all four "d-d" transitions, in agreement with the views of some previous workers, but contrary to those of others who have suggested that only three "d-d" bands were to be found in this region, the fourth being identified as a shoulder at ~ 26,000 cm^{-1}.

This conclusion is in good accord with the esr results. The observed g values ($g_z = 2.244$, $g_x = g_y = 2.051$) are nearly the same as those[7] for $Cu(AcAc)_2$ ($g_z = 2.264$, $g_x = g_y = 2.053$), and in both cases, using the appropriate molecular orbital coefficients, these data lead to the result that the $x^2 - y^2$, xz, and yz orbitals should lie within a range of ~5000 cm^{-1}.

Conclusive evidence that d_{z^2} also lies in this range, as indicated by the MO calculation, is provided by the polarized spectra, measured at 25°. Figure 1 shows the absorption of light polarized in the directions of the x and y molecular axes;[15] it was constructed from the results of polarization measurements made on the 001, 100, and 110 faces of crystalline $Cu(DPM)_2$. None of the absorption in the range 450–800 mμ had principally z polarization; thus the absorption is all in-plane polarized. It is evident from Figure 1 that the visible absorption of $Cu(DPM)_2$ consists of *four* overlapping bands, whose maxima occur at ~20,000, ~18,200, ~16,400, and ~15,600 cm^{-1}.

Finally, it may be noted that the assignment of the near-ultraviolet spectrum, which consists of three distinct maxima, at 48,600, 40,000, and ~33,500 (doublet) as well as a shoulder at ~26,000 cm^{-1}, has been reconsidered on the basis of the results of the MO calculation and some rough indications of polarizations obtained using hopper crystals. The doublet around 33,500 cm^{-1} is again assigned as two close π–π^* transitions, in agreement with the conclusions of nearly all previous workers. The band at 40,000 cm^{-1} appears most likely to be due to a transition from a ligand σ orbital to the d_{xy} orbital, as previously proposed.[11] The band at 48,600 cm^{-1}, for which a π–π^* assignment had previously been proposed by some[11,12] but rejected by other workers,[18] is now assigned as a d_{yz} to π^* band. The 26,000-cm^{-1} absorption is attributed to another ligand σ to d_{xy} transition.

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[15] Molecular Cartesian axes are defined throughout so that z is perpendicular to the molecular plane, x bisects O–Cu–O angles within the chelate rings, and y bisects O–Cu–O angles between different chelate rings. The molecular symmetry is D_{2h}.

[16] With the collaboration of Dr. C. B. Harris.

[17] The designations "d_{ij}" or "d orbital" are used here for brevity to denote molecular orbitals of which the indicated Cu d orbital constitutes the major part.

[18] L. S. Forster, *J. Am. Chem. Soc.*, **86**, 3001 (1964).

F. Albert Cotton, John J. Wise
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Received May 12, 1966

Organic Syntheses by Means of Noble Metal Compounds. XXVII.[1] Decarbonylation of Acyl Halides Catalyzed by a Rhodium Complex and Preparation of Acylrhodium Complexes by a Novel Addition Reaction of Acyl Halides

Sir:

We have reported that aldehydes can be decarbonylated smoothly at room temperature by the reaction with chlorotris(triphenylphosphine)rhodium.[2] The decarbonylation of acyl halides with the same complex again gives smooth decarbonylation under mild conditions to yield olefins, hydrogen chloride, and chlorocarbonylbis(triphenylphosphine)rhodium. When it was impossible to form olefins, alkyl or aryl chloride was the product. Thus this reaction is a very efficient and

$$RCH_2CH_2COCl + RhCl(Ph_3P)_3 \longrightarrow RCH{=}CH_2 + HCl + RhClCO(Ph_3P)_2$$

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[1] Part XXVI: J. Tsuji and N. Iwamoto, in preparation.

[2] J. Tsuji and K. Ohno, *Tetrahedron Letters*, No. **44**, 3969 (1965).