from the Notre Dame Radiation Laboratory.

Registry No. Fe^{II}(PTS)$^{4-}$, 69087-62-3; Co^{II}(PTS)$^{4-}$, 67462-30-0; Co^{III}(PTS)$^{3-}$, 69087-63-4; Co^{III}(PTS)(H$_2$O)Cl^{4-}, 69028-14-4; Co^{III}(PTS)Cl$_2$$^{5-}$, 69028-15-5; Co^{III}(PTS)(H$_2$O)I^{4-}, 69056-52-6; Co^{III}(PTS)I$_2$$^{5-}$, 69028-16-6; Co(PTS)(H$_2$O)(SCN)$^{4-}$, 69028-17-7; Co(PTS)(SCN)$_2$$^{5-}$, 69042-79-1; Co(PTS)(H$_2$O)(N$_3$)$^{4-}$, 69028-18-8; Co(PTS)(N$_3$)$_2$$^{5-}$, 69028-19-9; Fe(PTS)(OH$_2$)$_2$$^{5-}$, 69028-20-2; [Co-(PTS)(OH$_2$)$_2$$^{3-}$,Cr(bpy)$_3$$^{3+}$], 69028-25-7; [Co(PTS)(OH$_2$)$_2$$^{3-}$,Ru-(bpy)$_3$$^{2+}$]$^-$, 69028-26-8; [Co(PTS)(OH$_2$)$_2$$^{4-}$,Cr(bpy)$_3$$^{3+}$]$^-$, 69028-28-0; [Co(PTS)(Cl)$_2$]Na$_5$, 69028-21-3; [Co(PTS)(Br)$_2$]Na$_5$, 69028-22-4; [Co(PTS)(NCS)$_2$]Na$_5$, 69028-23-5; [Co^{II}(PTS)$^{4-}$,Ru(bpy)$_3$$^{2+}$]$^{2-}$, 69028-30-4.

Supplementary Material Available: Figure 1 showing transformations in the absorption spectrum of cobalt(III) and cobalt(II) sulfophthalocyanines and Table I with analytical data for acidocobalt(III) sulfophthalocyanines (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) G. Ferraudi and E. Srisankar, *Inorg. Chem.*, **17**, 3164 (1978).
(2) Ligand abbreviations: (PTS)$^{6-}$, phthalocyaninetetrasulfonate hexaanion; (PTS)$^{5-}$, one-electron-oxidized radical; (PTS)$^{7-}$, one-electron-reduced radical; (PTSH)$^{5-}$, hydrogenated derivative with the same oxidation state as (PTS)$^{6-}$.
(3) Y. Harel and J. Manassen, *J. Am. Chem. Soc.*, **99**, 5817 (1977).
(4) Y. Harel, J. Manassen, and H. Lavanon, *Photochem. Photobiol.*, **23**, 337 (1976).
(5) P. Day, H. A. O. Hill, and M. G. Price, *J. Chem. Soc. A*, 90 (1968).
(6) G. Ferraudi and J. F. Endicott, *J. Am. Chem. Soc.*, **99**, 243 (1977).
(7) C. Y. Mok and J. F. Endicott, *J. Am. Chem. Soc.*, **99**, 1276 (1977), and references therein.
(8) R. T. Taylor, L. Smucker, M. L. Hanna, and J. Gill, *Arch. Biochem. Biophys.*, **156**, 521 (1973).
(9) Although it is accepted that $\pi-\pi^*$ transitions make the main contribution to the absorption spectrum of the phthalocyanines, the authors do not agree on the order of the excited states which are populated in these transitions; e.g., see ref 10. Moreover, charge-transfer transitions with a metal-to-ligand character have been assigned for various iron(II) sulfophthalocyanine complexes and cobalt(I) sulfophthalocyanine; see for example: M. Whalley, *J. Chem. Soc.*, 866 (1964); B. W. Dale, *J. Chem. Soc.*, 331 (1968); ref 5.
(10) A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 65 (1965).
(11) C. A. Parker and G. E. Hatchard, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1965).
(12) G. Ferraudi, J. F. Endicott, and J. Barber, Jr., *J. Am. Chem. Soc.*, **97**, 6406 (1975).
(13) G. Ferraudi, *Inorg. Chem.*, **17**, 1370 (1978).
(14) J. H. Weber and D. H. Busch, *Inorg. Chem.*, **4**, 469 (1965).
(15) J. Fries, "Trace Analyses", E. Merk, Darmstadt, 1971.
(16) G. Ferraudi, *Inorg. Chem.*, **17**, 1370 (1978).
(17) W. Wolfrom, *Methods Carbohydr. Chem.*, **1** (1962).
(18) B. R. Baker and B. D. Mehta, *Inorg. Chem.*, **4**, 848 (1965).
(19) K. Bernaver and S. Fallab, *Helv. Chim. Acta*, **44**, 1728 (1961).
(20) A. R. Monahan, J. A. Brado, and A. F. DeLuca, *J. Phys. Chem.*, **76**, 446 (1972).
(21) A very intense absorption, $\epsilon \sim 10^5$ M^{-1} cm^{-1}, is observed at $\lambda_{max} \sim 680$ nm in the absorption spectra of the monomeric sulfophthalocyanines.[19] This is a very noticeable difference with the absorption spectrum of the dimeric species.[19,20] Moreover, both the differences in the absorption spectra of the monomeric and dimeric species and the dependence of the association equilibrium in medium conditions[20] suggest that a large component of the dimer may be due to ligand–ligand interactions. This will compensate the Coulombic repulsion of the sulfonate groups.
(22) Supplementary material.
(23) Anation equilibria have been observed in related systems. See for example: J. J. Watkins and A. Balch, *Inorg. Chem.*, **14**, 2720 (1965); D. V. Stynes and B. R. James, *J. Am. Chem. Soc.*, **96**, 2733 (1974); E. B. Fleischer, S. Jacobs, and L. Mestichelli, *ibid.*, **90**, 2527 (1968); R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, **14**, 886 (1975).
(24) L. D. Rollman and R. T. Imamoto, *J. Am. Chem. Soc.*, **90**, 1455 (1968).
(25) A. E. Cahill and H. Taube, *J. Am. Chem. Soc.*, **73**, 2847 (1951).
(26) C.-Y. Li and D.-H. Chin, *Anal. Lett.*, **8**, 291 (1975).
(27) Failures in the deaeration of the solution gave values of the product yields which were larger than the limit reported above.
(28) The long life of ^{2}E Cr(bpy)$_3$$^{3+}$ allows a dynamic quenching of this species by bulk sulfophthalocyanine. However, this process makes a very small contribution to the overall reaction under the experimental conditions indicated above.
(29) See ref 10, ESR spectra, p 78–80.
(30) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, London, 1970.
(31) J. F. Endicott, *Concepts Inorg. Photochem.*, 104–134 (1975).
(32) G. J. Ferraudi and J. F. Endicott, *J. Phys. Chem.*, **80**, 949 (1976).
(33) Complexation and disproportionation of iodine radicals: I$^-$ + I$\cdot$ $\rightleftharpoons$ I$_2^-$, k = 1.1 × 10^5; I$\cdot$ + I$\cdot$ $\rightarrow$ I$_2$, k = 10 × 10^9 M^{-1} s^{-1}; I$_2^-$ + I$_2^-$ $\rightarrow$ I$_3^-$, k = 9 × 10^9 M^{-1} s^{-1} [J. K. Thomas, *Adv. Radiat. Chem.*, **1**, 1.03 (1969); I. M. Grossweiner and M. Matheson, *J. Phys. Chem.*, **61**, 1089 (1957)].
(34) Complexation and disproportionation of thiocyanate radicals: SCN$\cdot$ + SCN$^-$ $\rightleftharpoons$ (SCN)$_2^-$, k = 2.0 × 10^5; SCN$\cdot$ + SCN$\cdot$ $\rightarrow$ (SCN)$_2$, k = 5.0 × 10^9; (SCN)$_2^-$ + (SCN)$_2^-$ $\rightarrow$ (SCN)$_2$ + 2SCN$^-$, k = 2.1 × 10^9 [M. Schoneshofer and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **74**, 393 (1970); J. H. Baxendale and D. A. Stott, *Proc. Chem. Soc., London*, 699 (1967); J. A. Baxendale, P. L. T. Bevan, and D. A. Stott, *Trans. Faraday Soc.*, **64**, 2389 (1968)].
(35) J. F. Myers, G. W. Rayner Canham, and A. B. P. Lever, *Inorg. Chem.*, **14**, 461 (1975).

Ligand Field Parameters and Photochemistry from Charge-Transfer Excited States of Bis[o-phenylenebis(dimethylarsine)]iron(III) Halides

JEFFREY I. ZINK,* PO-HSIN LIU, and BETSY ANFIELD

The charge-transfer spectroscopy and photochemistry of the title compounds Fe(das)$_2$XY$^+$ (X$^-$, Y$^-$ = Cl$^-$, Br$^-$, I$^-$) are reported. The d-orbital energies are determined from the arsine-to-iron charge-transfer spectra. Ligand field and angular overlap parameters are calculated from the charge-transfer spectra and compared to those of other first-row transition-metal(III) compounds. Fe(das)$_2$Cl$_2^+$ reacts photochemically in the presence of organoiodides to produce Fe(das)$_2$ClI$^+$ with quantum yields on the order of 10^{-3}.

The electronic spectroscopy and photochemistry of metal complexes containing ligands having low optical electronegativity are not well understood. Accurate determination of the ligands' spectrochemical properties is frequently prevented by low-energy ligand-to-metal charge-transfer absorption bands which obscure the ligand field transitions. Photoreactions from charge-transfer states include photoredox reactions and reactions of coordinated ligands for which detailed understanding is lacking. Recent spectroscopic and photochemical studies of charge-transfer excited states suggest that the photoreactions can be interpreted in terms of a

formally reduced metal center in ligand-to-metal charge-transfer (LTMCT) excited states[1-4] and a formally oxidized metal in metal-to-ligand charge-transfer (MTLCT) excited states.[5,6] However, many CT states transfer energy via intersystem crossing to lower lying ligand field states, and many are photoinactive.[1,7-9]

During spectroscopic and photochemical studies in this laboratory of metal complexes of bis[o-phenylenebis(dimethylarsine)], das, it was observed that the slightly photoactive *trans*-dihaloiron(III) complexes contained four well-resolved charge-transfer absorptions in addition to much
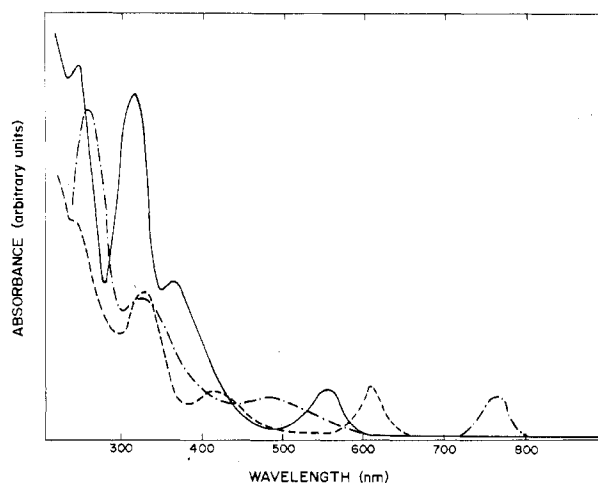
Figure 1. Charge-transfer electronic absorption spectra of Fe(das)$_2$X$_2^+$: X = Cl (—), X = Br (---), X = I (-·-).

less intense d–d transitions. The charge-transfer transitions offered the unusual opportunity not only to study the charge-transfer excited states but also to obtain the d-orbital energies and thus calculate the ligand field parameters. The results of electronic absorption spectroscopic studies and photochemical studies are reported here.

Experimental Section

Compounds. [Fe(das)$_2$Cl$_2$]Cl and [Fe(das)$_2$Br$_2$]Br were prepared and isolated using literature procedures.[10] [Fe(das)$_2$I$_2$]Cl was prepared in solution by the reaction of the dichloro or dibromo complex with iodoform. The diiodo complex decomposed within several minutes. The mixed dihalo compounds were prepared in solution by the reaction of Fe(das)$_2$NOX (X = Cl, Br, I) with iodoform[6] and by reaction of the dichloro or dibromo complexes with organohalides.

Spectroscopic Studies. All electronic absorption studies were carried out in acetone doubly distilled from Drierite. Spectra were recorded with a Cary 14 spectrometer. Luminescence from the solids was searched for at room temperature and at 77 K using a Spex fluorolog spectrofluorimeter.

Photochemistry. The electronic absorption spectra were taken on a Cary 14 spectrometer. The actinometry system was monitored on a Hitachi Perkin-Elmer 139 UV–vis spectrometer.

Photolysis was done with a Hanovia 100-W high-pressure quartz mercury-vapor lamp with filters isolating the 546-nm region. The filter combination consisted of a double-Pyrex plate, a chemical filter of 5 × 10^{-4} M aqueous K$_2$[CrO$_4$], and Corning filters 29-4 and 36-78. This combination isolated the 510–565-nm wavelengths with a 23.4% transmittance at 546 nm.[1,3]

An optical bench with mounted source, filters, and cells was used to measure all quantum yields. The samples were irradiated in 1-cm cylindrical cells with a 2.5-mL volume. The average photon flux on the surface of the cell was 2.3 × 10^{15} *hv*/s ± 3%. Actinometry was carried out at the beginning and end of each run with Reinecke's salt.[11] The quantum yields were calculated[12] by monitoring both the disappearance of the charge-transfer band of the starting material at 533 nm and the appearance of the charge-transfer band of the photoproduct at 675 nm.

Results and Discussion

1. Assignments of Charge-Transfer and Ligand Field Bands. The electronic absorption spectra of *trans*-dihalobis[*o*-phenylenebis(dimethylarsine)]iron(III) complexes, Fe-(das)$_2$XY$^+$, are dominated by four intense bands, ε >10^3 (Figure 1). The energies of these bands for the dichloro, -bromo, and -iodo complexes as well as for the mixed halo complexes are given in Table I. In addition to the intense features, the absorption spectra contain weak features (ε <100) in the UV, visible, and near-IR regions of the spectrum which generally appear as shoulders on the intense features.

The four intense absorption bands are assigned to internal ligand and charge-transfer transitions on the basis of the large molar absorptivities and their quantitative relationships with

Table I. Energies of CT Band Maxima for Fe(das)$_2$XY$^+$

X	Y	absorption band maxima (10^3 cm^{-1})			
		I	II	III	IV
Cl	Cl	18.1	27.1	31.5	40.0
Br	Br	16.5	24.4	30.8	38.6
I	I	13.0	21.1	30.5	38.4
Cl	Br	17.4	25.8	31.1	40.0
Cl	I	14.8	24.8	31.5	38.2
Br	I	14.3	23.0		
Cl	Br	17.3^a	25.5^a		
Cl	I	15.5^a	23.9^a		
Br	I	14.8^a	22.9^a		

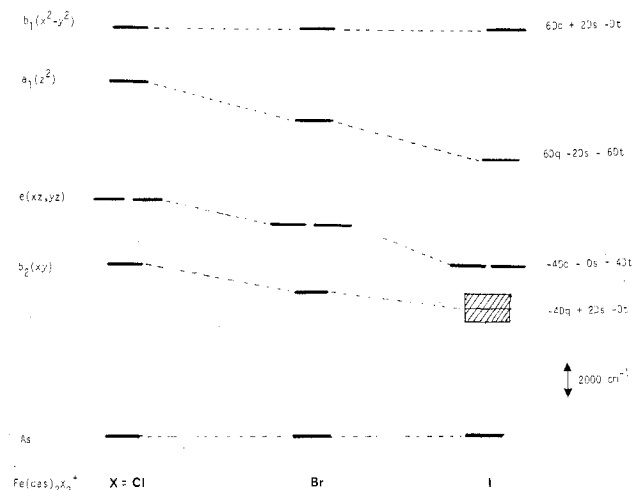^{a} Calculated using the ligand field parameters given in Table IV. See text for discussion.

Figure 2. Quantitative orbital energy level diagram for Fe(das)$_2$X$_2^+$ complexes. The tetragonal ligand field parameters are given on the right.

the d–d bands (vide infra). In the case of the charge-transfer transitions, both ligand-to-metal charge transfer (LTMCT) and metal-to-ligand charge transfer (MTLCT) must be considered. The latter can be discounted for the low-energy CT because of the iron oxidation state of 3+. The lowest energy LTMCT band(s) is (are) expected to be das to iron based on the optical electronegativities of the ligands (Cl$^-$, 3.0; Br$^-$, 2.8; I$^-$, 2.5; das, 2.46).[13] As discussed below, the only consistent assignment for all the CT bands is das (or an orbital primarily das in character) to iron.

The three lowest energy charge-transfer bands, labeled bands I–III in Table I, are assigned to the transitions to d$_{xz}$ and d$_{yz}$ (band I), to d$_{z^2}$ (band II), and to d$_{x^2-y^2}$ (band III). These assignments are summarized in the quantitative energy-level diagram shown in Figure 2. The observed changes in the energies of the CT bands as the halides are changed are caused by the changed energies of the d orbitals as the ligand field varies. The ligand field properties responsible for these changes will be quantitatively calculated in the next section. If any of these bands were transitions from the halide to metal d orbitals, the energy changes caused by changing the halide should be much larger. On the basis of optical electronegativity, a halide-to-metal CT should decrease 6 × 10^3 cm^{-1} as Cl is replaced by Br and 9 × 10^3 cm^{-1} if Br is replaced by I. Furthermore, in the mixed dihalo complexes, CT bands from both of the different halides could be expected if orbital mixing were small. No new bands are found in the mixed dihalo complexes. Because halide and arsine orbitals are basis functions for the same irreducible representations in D_{2h} symmetry, the CT is best stated as (As + X) to Fe(III).

The highest energy transition, band IV, is assigned to an internal ligand transition in the das ligand. The most telling

Table II. Ligand Field States of Fe(das)₂X₂⁺ and Partial Assignments

electron configs	state symmetry (in D_{4h})	energies for X = Cl		energies for X = Br	
		calcd[a]	obsd	calcd[a]	obsd
$b_2{}^2e^3$	^2E	ground state		ground state	
$b_2{}^1e^4$	$^2B_2$	$(5.0)^b$	5.0	$(5.0)^b$	5.0
$b_2{}^2e^2a_1{}^1$	$^2A_1, {}^2A_2,$	8.5	8.0–10.0	7.9	7.5–9.5
	$^2B_1, {}^2B_2$				
$b_2{}^2e^2b_1{}^1$	$^2A_1, {}^2A_2,$	13.5	11.8–14.5	12.9	11.0–13.5
	$^2B_1, {}^2B_2$				
$b_2{}^1e^3a_1{}^1$	$^2E, {}^2E$	13.5	11.8–14.5	12.9	11.0–13.5
$b_2{}^1e^3b_1{}^1$	$^2E, {}^2E$	18.5	19.4	19.3	

[a] Calculated using the one-electron orbital energies and neglecting electron repulsion. All energies in units of 10^3 cm⁻¹.
[b] Determined directly from the d–d absorption.

evidence for this assignment is the constancy of its energy in all of the compounds in Table I ((39 ± 1) × 10^3 cm⁻¹). In addition, the free ligand has an absorption shoulder at 36 × 10^3 cm⁻¹ in ethanol and the analogous Co^III(das)₂Cl₂⁺ complex has an absorption maximum at 40 × 10^3 cm⁻¹.[14]

The assignment of the d–d bands is complicated by the presence of 14 states of the 6 configurations arising from the one-electron transitions, by the large number of these states mixed by configuration interaction, by the selection rules in the idealized D_{4h} symmetry in which all 14 transitions are vibronically allowed, and by the obscuration of the d–d bands by the CT bands. The 14 states arising from the one-electron transitions are listed on the left of Table II. Because few of the peaks are resolved in the absorption spectra and because some are obscured by the CT absorptions, neither the LF band assignments nor a determination of the LF parameters Dq, Ds, or Dt can be carried out using direct spectral-fitting procedures.[15]

The assignment of many of the spin-allowed d–d bands can be accomplished utilizing the one-electron d-orbital energies determined from the CT spectra shown in Figure 2. On the basis of the CT assignments, the energy difference between the $e(d_{xz}, d_{yz})$ and $a_1{}^1(d_{z^2})$ orbitals in the dichloro complex is (27.1–18.1) or 9.0 × 10^3 cm⁻¹. Thus, the calculated one-electron d–d transition energy $b_2{}^2e^3 \rightarrow b_2{}^2e^2a_1{}^1$ is 9.0 × 10^3 cm⁻¹. Similarly, the calculated transition energy $b_2{}^2e^3 \rightarrow b_2{}^2e^2b_1{}^1$ is 31.5–18.1 or 13.4 × 10^3 cm⁻¹. The b_2 orbital energy is not obtained from the CT spectra because the orbital is filled. Thus the one-electron d–d transitions from b_2 cannot be calculated from the CT data alone. The lowest energy d–d transition, however, is $b_2 \rightarrow e$ and is expected to be in the near-IR region of the spectrum. If this transition energy is E, then the transition $b_2{}^2e^3 \rightarrow b_2{}^1e^3a_1{}^1$ will have energy (9.0 + E) × 10^3 cm⁻¹ and $b_2{}^2e^3 \rightarrow b_2{}^1e^3b_1{}^1$ will have energy (13.4 + E) × 10^3 cm⁻¹. These calculated energies are apparent from Figure 2. The lowest energy transition is observed at 5 × 10^3 cm⁻¹ both in the solution absorption spectrum and in the solid-state reflectance spectrum of the chloro and bromo complexes.[16] Using the value $E = 5 \times 10^3$ cm⁻¹, we have calculated the one-electron d–d transition energies, and the results are given in Table II.

The energies of the spectroscopically observed transitions are related to the one-electron energies calculated above. However, electron repulsion and configuration interaction between the states will respectively increase the number of transitions over that expected on a one-electron basis and shift the state energies. A simple example illustrating these aspects is found in the doublet states of the $b_2{}^2e^2a_1{}^1$ configuration. The pair of electrons in the e orbital can be spin paired in the d_{xz} orbital or the d_{yz} orbital, can be spin "up" in the d_{xz} orbital and spin "down" in the d_{yz} orbital or vice versa, or can be both spin "up" or both spin "down" with one each in d_{xz} and d_{yz}. These configurations give rise to $^2A_1$, $^2A_2$, $^2B_1$, and $^2B_2$ states

with different energies because of the different electron repulsions in the different configurations. Thus four transitions are expected whose energies depend on the electron-repulsion integral. In addition, the $^2B_2$ state, for example, can mix with $^2B_2$ state from the $b_2{}^2e^2b_1{}^1$ configuration. For these reasons, the $b_2{}^2e^2a_1{}^1$ configuration will not give rise to a single state at 8.5 × 10^3 cm⁻¹ but instead will give rise to four states with a spread of energies in the vicinity of 8.5 × 10^3 cm⁻¹.

Few of the d–d transitions can be resolved in the electronic absorption spectrum. The only well-resolved d–d features are at 5.0 and 14.5 × 10^3 cm⁻¹. A moderately well-separated shoulder is found at 19.4 × 10^3 cm⁻¹ and a series of broad features are found between (8–10) and (12–14) × 10^3 cm⁻¹. Even though the individual states cannot be assigned, the one-electron configurations can be associated with the absorption features as shown in Table II.

Luminescence of the Fe(das)₂X₂⁺ compounds would be expected to occur in the IR with an emission maximum at wavelengths longer than 10 000 Å if the lowest excited state emitted. We do not have sensitive enough detectors to observe such emission if it occurs. The possibility that luminescence could occur from the charge-transfer states was tested. Not surprisingly, no luminescence was observed between 3500 and 8000 Å for solids or solutions at room temperature or at 77 K.

2. Ligand Field Parameters. The tetragonal crystal field parameters Dq, Ds, and Dt,[17] the McClure parameters $\delta\sigma$ and $\delta\pi$,[18] and the angular overlap model's (AOM) l_σ and l_π[19] are usually determined by computer simulations of ligand field spectra.[15] The best studied systems include d^3 Cr(III), d^8 Ni(II), and d^6 Co(III), while studies of d^5 Fe(III) are rare.[15] The difficulties encountered in the latter system include the large number of poorly resolved bands and complications from charge-transfer transitions.

Ideally, the *ligand field* parameters can be determined from *charge-transfer* spectra. The conditions which must be met are: (1) transitions to (or from) all of the d orbitals must be observed in the CT spectrum and (2) the differences between the electron repulsion integrals in the charge-transfer energies must be small. Under these conditions, the one electron d-orbital energies can be calculated, and from them the ligand field parameters can be determined. In the case of the Fe(das)₂XY⁺ compounds, condition (1) is not fulfilled because the CT transition to the filled b_2 (d_{xy}) orbital is not observed. Fortunately, the energy spacing between b_2 and e can be accurately determined from the well-resolved band in the d–d spectrum and thus all of the required one-electron d-orbital energies can be calculated. The electron-repulsion integrals are more difficult to evaluate, but the difference between them in the CT transitions to the various metal d orbitals should be small because the interaction between the formally oxidized ligand "core" and the various d orbitals will be similar. The crucial feature, that the d-orbital energy differences be obtained, is satisfied. Further confirmation is obtained from the self-consistency of the ligand field calculation below.

Consider first the evaluation of the crystal field parameters. The energies of the one-electron orbitals expressed in terms of the crystal field parameters are shown in Figure 2. The values of Dq, Ds, and Dt are obtained by solving four simultaneous equations obtained from the energy differences between the orbitals[17] (eq 1). Results are given in Table III.

$$4Ds + 5Dt = E(x^2 - y^2) - E(z^2) \tag{1a}$$

$$-3Ds + 5Dt = E(xz, yz) - E(xy) \tag{1b}$$

$$-Ds - 10Dt + 10Dq = E(z^2) - E(xz, yz) \tag{1c}$$

$$10Dq = E(x^2 - y^2) - E(xy) \tag{1d}$$

Table III. Ligand Field Parameters[a]

	$Fe(das)_2Cl_2^+$	$Fe(das)_2Br_2^+$	$Fe(das)_2I_2^+$
Dq	18.4 ± 1	19.3 ± 1	22.5 ± 2
Ds	-0.086 ± 0.005	0.20 ± 0.005	0.63 ± 0.3
Dt	0.97 ± 0.08	1.12 ± 0.05	1.37 ± 0.2
l_σ^X	8.3 ± 0.4	$7.0_7 \pm 0.3$	$5.4_7 \pm 0.3$
l_π^X	$5.7_7 \pm 0.3$	$5.3_7 \pm 0.3$	4.5 ± 1
l_σ^{As}	10.5 ± 0.5	$10.2_7 \pm 0.5$	$10.1_7 \pm 0.5$
l_π^{As}	$3.2_8 \pm 0.2$	$2.8_8 \pm 0.1$	2.0 ± 0.5

[a] All energies are in units of 10^3 cm^{-1}. The experimental uncertainties are largest for the diiodo complex because of the large uncertainty in the energy of the b_2 orbital.

The parameters of the angular overlap model were calculated using the data in Figure 2 and the expressions

$$E(x^2 - y^2) = 3l_\sigma^{As} \tag{2a}$$

$$E(z^2) = 2l_\sigma^X + l_\sigma^{As} \tag{2b}$$

$$E(xz,yz) = 2l_\pi^X + 2l_\pi^{As} \tag{2c}$$

$$E(xy) = 4l_\pi^{As} \tag{2d}$$

The values of l_σ^{As} and l_π^{As} were obtained from the CT transition energies to the $d_{x^2-y^2}$ and d_{xy} orbitals, respectively. The values of l_σ^X and l_π^X were then calculated from the d_{z^2} and d_{xz},d_{yz} orbitals. The results of these calculations are given in Table III.

Note that the procedure used to calculate the angular overlap model parameters assumes that the HOMO is the zero-energy origin of the energy scale. The origin which should be used is that of the unperturbed d orbitals. If the energy difference between these origins is W, the observed transition energies in the CT spectrum are those of eq 2a–d plus W. The l_σ values shown in Table III are thus $l_\sigma + W/3$ and $l_\pi + W/4$. The value of W cannot be determined from the absorption spectra. Its upper limit calculated from the b_2 orbital of $Fe(das)_2I_2^+$ is 8×10^3 cm^{-1}.

The angular overlap parameters are related to the crystal field parameters by the expressions[20]

$$Ds = \tfrac{2}{7}(l_\sigma^{As} - l_\sigma^X) + \tfrac{2}{7}(l_\pi^{As} - l_\pi^X) \tag{3a}$$

$$Dt = \tfrac{6}{35}(l_\sigma^{As} - l_\sigma^X) - \tfrac{8}{35}(l_\pi^{As} - l_\pi^X) \tag{3b}$$

$$Dq = 3l_\sigma^{As} - 4l_\pi^{As} \tag{3c}$$

In order to test the consistency of the assignments, Dq, Ds, and Dt were calculated using the AOM parameters in Table III. The Dq values for the Cl, Br, and I complexes from eq 3 are 18.3 (8), 19.2 (9), and 22.5 (1) $\times 10^3$ cm^{-1} compared to the measured values of 18.4, 19.3, and 22.5 $\times 10^3$ cm^{-1}. The Ds values were, respectively, -0.082 (8), 0.20 (3), and 0.62 (9) compared to -0.085 (7), 0.20, and 0.62 (8). Note that in these calculations, W cancels out. These relationships provide a bonding interpretation of the crystal field parameters (vide infra). In addition, they show that the two sets of calculations are self-consistent.

The energies of the CT transitions in mixed dihalo complexes can be predicted if we assume that the AOM parameters are additive. The calculated transition energies are compared to the observed energies at the bottom of Table I. Note that the average deviation between the calculated and observed transition energies is 13 nm.

Several trends in the parameters and comparisons with parameters calculated for other metal systems are of interest. First, the average value of Dq found in this study for the das ligand is 2050 cm^{-1}. The average value of Dq calculated for the analogous $Cr(das)_2X_2^+$ compounds using the d–d bands was 2040 cm^{-1},[21] For $Fe^{II}(das)_3^{2+}$, the calculated Dq was 2490 cm^{-1}.[21] These results are in accord with the observation of Feltham et al. that the spectrochemical properties of das are similar to those of ethylenediamine in highly charged com-

Table IV. Photochemical Results

$[Fe(das)_2Cl_2^+]$, M	RI	[RI], M	$\phi^{a,b}$
5.50×10^{-4}	CH$_3$I	1.2×10^{-2}	4.7×10^{-4}
2.68		1.2×10^{-2}	5.2
2.90		1.84×10^{-2}	4.5
2.56		4.69×10^{-2}	4.9
4.0×10^{-4}		4.10×10^{-4}	$<10^{-4}$
2.9×10^{-4}	CH$_3$CHICH$_3$	5.4×10^{-3}	19×10^{-4}
2.9×10^{-4}		2.7×10^{-3}	21×10^{-4}
2.9×10^{-4}		6.0×10^{-4}	$<10^{-4}$

[a] Quantum yields accurate to $\pm 25\%$. [b] 546-nm irradiation.

plexes but that back-bonding plays a larger role when the positive charge on the metal decreases.[21] Note also that a small ligand inductive effect[22] is observed in $Fe(das)_2X_2^+$. As the axial ligand field decreases in the series Cl > Br > I, $10Dq$ for das increases.

Second, the trends in the tetragonal field parameters follow well-established orders. The increase of Dt in the series Cl > Br > I is as expected for the halides. The AOM parameters are more readily interpreted. The calculated l_π^X (X = Cl, Br, I) parameters, when normalized to those based on ammonia, are 0.91, 0.85, and 0.71 compared to the average values of 0.90, 0.85, and 0.65 with chromium(III) and cobalt(III).[23] The l_σ^X parameters are -1.2, -2.1, and -3.2 compared to -1.6, -2.1, and -2.6, respectively. These values, the first calculated for Fe(III) and based on the CT spectrum, are consistent both in the ordering and in the magnitude to those evaluated in the well-studied Cr(III) and Co(III) systems. The AOM parameters for das in the chloro complex normalized to those based on ammonia are $l_\sigma^{As} = +0.36$ and $l_\pi^{As} = +0.52$. These values place das as a slightly better σ-donating ligand than ethylenediamine and about equal in π-donating ability to water.

3. Photochemistry. During the spectroscopic studies it became apparent that $Fe(das)_2Cl_2^+$ photochemically reacted with alkyl halides to produce mixed halo $Fe(das)_2XY^+$ compounds. Similar reactivity had previously been observed upon LTMCT of tris(dithiocarbamato)iron(III) systems where the formally reduced iron in the CT excited state scavenged halogens from alkyl and aryl halides.[2] However, photoactivity from the das system was surprising because the lowest lying excited state is only 5×10^3 cm^{-1} above the ground state and efficient radiationless deactivation to the ground state is expected. Photoreaction quantum yields were measured to determine the efficiency of the photoactivity.

Photolysis of $Fe(das)_2Cl_2^+$ in dry methanol and acetone with added iodoform or 2-iodopropane causes the CT bands of the reactant to disappear and those of the $Fe(das)_2ClI^+$ photoproduct to appear with a 1:1 stoichiometry and isobestic points at 437, 486, and 583 nm. Continued photolysis produces unstable $Fe(das)_2I_2^+$ which thermally decomposes in a few minutes with loss of all CT absorption bands above 400 nm. Photolysis in the presence of LiCl causes disappearance of all absorption bands above 450 nm. No significant photochemical reactions were observed with iodobenzene or iodoethane. In the presence of the radical initiator benzoyl peroxide, unirradiated $Fe(das)_2Cl_2^+$ first produces $Fe(das)ClI$ and further reacts to form $Fe(das)_2I_2^+$ which then decomposes. Decomposition with loss of all absorption above 450 nm occurs when photolysis is carried out in acetone with no other reactants and is enhanced in the presence of benzoyl peroxide.

The results of the quantitative photochemical studies are summarized in Table IV. The organic halides do not absorb in the vicinity of 546 nm but have intense bands in the 360-nm region of the second CT band of the complex. The measured quantum yields are accurate to within 25% because of competition from the thermal reaction and because of the low photoreactivity.

The photoreaction pathway can be interpreted in terms of excited-state bonding changes. In the directly populated CT state, iron–chlorine π bonding is weakened because of population of the antibonding d_{xz} and d_{yz} metal orbitals. In addition, the iron is formally reduced. The weakened iron–chlorine coordination site probably undergoes radical attack by the iodine with homolytic cleavage of the coordinated chlorine. This radical pathway is consistent with the enhanced thermal reactivity in the presence of the radical initiator benzoyl peroxide. In addition, the trend exhibited by the photoreaction with the organic halides $CH_3CHICH_3 > CH_3I_3 > C_5H_5I \geq C_6H_5I$ is consistent with the bond energies of those halides.[24]

References and Notes

(1) A. W. Adamson and P. D. Fleischauer, "Concepts of Inorganic Photochemistry", Wiley-Interscience, New York, N.Y., 1975.
(2) D. P. Schwendiman and J. I. Zink, *J. Am. Chem. Soc.*, **98**, 4439 (1976).
(3) P. H. Liu and J. I. Zink, *J. Am. Chem. Soc.*, **99**, 2155 (1977).
(4) G. L. Miessler, G. Stuck, T. P. Smith, K. W. Given, M. C. Palazzotto, and L. H. Pignolet, *Inorg. Chem.*, **15**, 1982 (1976).
(5) K. R. Mann, H. B. Gray, and G. S. Hammond, *J. Am. Chem. Soc.*, **99**, 306 (1977).
(6) P. H. Liu and J. I. Zink, *Inorg. Chem.*, **16**, 3165 (1977).
(7) G. Malouf and P. C. Ford, *J. Am. Chem. Soc.*, **96**, 601 (1974).
(8) M. S. Wrighton, H. B. Abrahamson, and D. L. Morse, *J. Am. Chem. Soc.*, **98**, 4105 (1976).
(9) M. J. Incorvia and J. I. Zink, *Inorg. Chem.*, **17**, 2250 (1978).
(10) R. S. Nyholm, *J. Chem. Soc.*, 851 (1950).
(11) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
(12) R. M. Dahlgren and J. I. Zink, *Inorg. Chem.*, **16**, 3154 (1977).
(13) C. K. Jørgensen, *Prog. Inorg. Chem.*, **12**, 101 (1970).
(14) S. Yamada, *Coord. Chem. Rev.*, **2**, 83 (1967).
(15) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).
(16) W. Silverthrone, Ph.D. Thesis, University of Arizona; R. D. Feltham, private communication.
(17) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962.
(18) D. S. McClure, "Advances in Chemistry Coordination Compounds", S. Kirshner, Ed., Macmillan, New York, N.Y., 1961.
(19) C. K. Jørgensen, R. Pappalardo, and H. H. Schmidtke, *J. Chem. Phys.*, **39**, 1422 (1963).
(20) M. Keeton, B. F. Chou, and A. B. P. Lever, *Can. J. Chem.*, **49**, 192 (1971).
(21) R. D. Feltham and W. Silverthorn, *Inorg. Chem.*, **7**, 1154 (1968).
(22) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967); **7**, 795 (1968).
(23) L. G. Vanquickenborne and A. Ceulemans, *J. Am. Chem. Soc.*, **99**, 2208 (1977).
(24) E. Huyser, "Methods in Free-Radical Chemistry", Marcel Dekker, New York, N.Y., 1969, pp 89–139.

Determination of the Comproportionation Constant for a Weakly Coupled Mixed-Valence System by Titration of the Intervalence Transfer Band: μ-(4,4'-Bipyridyl)-bis(pentaammineruthenium)(5+)

JAMES E. SUTTON, PATRICK M. SUTTON, and HENRY TAUBE*

The change in absorbance in the region of the intervalence transition for μ-4,4'-bipyridyl-bis(pentaammineruthenium) when the fully oxidized state is titrated with a reducing agent is used to obtain the comproportionation constant for reaction I. This value (24 ± 1 at 19.0 °C) was used to calculate the extinction coefficient (8.8×10^2 M^{-1} cm^{-1}) at the band maximum (1030 nm in D$_2$O) and the oscillator strength corresponding to the transition. The stabilization resulting from electron delocalization in turn is calculated from the oscillator strength as 48 cal and falls far short of the stability of the mixed-valence compared to the isovalent state, which amounts to 5×10^2 cal. It seems likely that the major contribution to the stability of the mixed-valence state is the electrostatic interaction between the positively charged ends, which will favor the mixed-valence state. Calculation of this contribution using the macroscopic dielectric constant for the solvent, however, falls far short of accounting for the experimental value. When, as in this case, the contribution to stability from electron delocalization is small, the measurements would seem to provide a rather direct way of exploring the electrostatic term.

Introduction

Over the last 10 years a large number of robust molecules containing two or more metals in different oxidation states have been prepared and studied.[1–6] One important property of these mixed-valence compounds is the intervalence transfer (IT) band corresponding to a light-induced charge transfer between the metal centers.[7,8] Hush has treated these IT bands theoretically[7,9] and concludes that their intensity provides information on the extent of communication between the metal centers. In addition, the energy of these bands is related to the Franck–Condon barrier to electron transfer provided coupling between the metal centers is not very strong.

This paper is based on a reinvestigation[3–5] of the μ-(4,4'-bipyridyl)-bis(pentaammineruthenium)(5+) ion which was undertaken to obtain quantitative data on the oscillator strength of the IT band. In the work on mixed-valence molecules done heretofore, values of the equilibrium quotient governing a reaction of the type

$$[2,2] + [3,3] = 2[3,2] \tag{I}$$
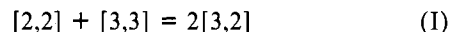
have been obtained from cyclic voltammetry data ([2,2], [3,2], and [3,3] represent the three different stages of oxidation for the binuclear species). Because the waves corresponding to the two redox stages overlap and because the waves even in well-behaved systems seldom have an ideal form, dependable values of the comproportionation[10] quotient, K_c, cannot be obtained from the electrochemical data unless K_c is greater than about 2×10^2. For some such systems, values of K_c have been estimated from the abnormally large peak to peak separations which can be observed when the waves coalesce, but in the absence of ideal behavior and of a theory even for the ideal cases connecting peak to peak separation with K_c,