

along one of the Ru-Cp bonds and in opposite directions along the other. Therefore the net bond length change along the Ru-Cp bond is 0.16 Å for one and 0.08 Å for the other.

Summary

The emission spectrum of ruthenocene contains unusually well-resolved vibronic structure. The crystal spectrum consists of two long progressions in the 333-cm⁻¹ metal-ring stretching mode, which are separated from each other by 165 cm⁻¹. Each of the peaks of the 333-cm⁻¹ progression contains sidebands that are repeated throughout the spectrum. This repetition is explained in terms of beats in the recurrence of overlaps in the time domain.

The complete spectrum is accurately calculated by using four displaced normal modes. The major displacement is along the metal-ligand bond axis with minor contributions from ring tilting modes. The point group of the emitting molecule has lower symmetry than that of the molecule in the ground state.

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Assignments of Ground- and Excited-State Spectra from Time-Resolved Absorption and Circular Dichroism Measurements of the ²E State of (Δ)-Cr(bpy)₃³⁺

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Time-resolved absorption and circular dichroism (CD) spectra of the ²E excited state of (Δ)-Cr(bpy)₃³⁺ are obtained, and assignments of both spectra are made. Excited-state absorption bands at 445 (ε ≈ 3800) and 385 nm (ε ≈ 8000) are assigned as due to the sum of intensity from both ligand-to-metal charge-transfer (LMCT) and metal-to-ligand charge-transfer (MLCT) transitions. Excited-state CD bands at 430 nm (Δε ≈ -8) and 334 nm (Δε ≈ -11) are also attributed to a sum of CD intensity from LMCT and MLCT transitions, while an excited-state CD band at 268 nm (Δε ≈ -26) is assigned as due solely to an LMCT transition. The magnitudes of the CDs in the ligand long-axis ππ* transitions are similar for the ²E excited state and the ⁴A₂ ground state. The excited-state absorption and CD spectra are consistent with a purely metal-centered description of the excited state. Reassignments of the ground-state absorption and CD spectra are made. Both ground- (⁴A₂) and excited-state (²E) CD spectra reveal transitions not seen in the unpolarized absorption spectra.

Introduction

The analysis of the circular dichroism (CD) spectra of stable chiral molecular species has long been important in understanding their properties.¹⁻⁵ In particular, information about molecular structure, transitions weak in absorption, and the interaction of molecular orbitals can be obtained from CD spectra. In principle, the same analysis of CD spectra is applicable to the CD spectra of transient molecular species, such as chiral intermediates in chemical reactions and the excited states of chiral molecules. However, one is limited, using conventional CD equipment, to looking at intermediates that live for milliseconds or longer. As most molecular excited states do not live this long, the analysis of the CD spectra of excited states obtained by using conventional equipment has been limited to the observation of a few triplet states of chiral organic aromatics.⁶⁻⁹

Our laboratory has developed a method for determining the CD spectra of short-lived molecular species, and it has been shown to be useful in obtaining CD spectra with nanosecond time resolution.^{10,11} Using this time-resolved circular dichroism (TRCD) method, we have previously reported the CD spectrum of the excited-state absorptions of (Δ)-Ru(bpy)₃²⁺ and (Δ)-Fe(bpy)₃²⁺.¹²⁻¹⁴ In these studies, we focused primarily on the magnitudes of the CD of the ligand ππ* bands, as these magnitudes reflect the nature of the excited states probed.¹²⁻¹⁴ For (Δ)-Ru(bpy)₃²⁺, the magnitude of the bpy ππ* CD decreased and a new, weak CD attributed to the ππ* band of bpy⁻ was seen, consistent with the lowest excited state being a single-ligand localized MLCT state. For (Δ)-Fe(bpy)₃²⁺ the magnitude of the ππ* CD is nearly the same in the ligand field excited state as it is in the ground state and no new ππ* CD bands were found, consistent with a metal-centered description of the excited state.

In the current work we report the CD spectrum of the excited-state absorption of (Δ)-Cr(bpy)₃³⁺. While the chemistry of the excited state of this complex has been extensively studied,¹⁵⁻²⁷

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its spectroscopy has not been studied in detail. It has been shown that the lowest excited state is 2E and that this state lives for 63 μ s in aqueous solution at 20 $^\circ$ C.^{15,16} Under conditions of monophotonic excitation, population of the 2E state takes place in less than 1 ps¹⁶⁻¹⁹ and the yield of the doublet under most conditions is 1.0.^{20,21} The unpolarized absorption spectrum of the 2E state has been previously reported from 700 to 350 nm,¹⁶ and the current work extends this spectrum to 250 nm. We reassign much of the ground-state absorption and CD spectra of (Δ) -Cr(bpy) $_3^{3+}$. In particular, we make specific charge-transfer assignments for many of the observed bands, as the possibility of such charge-transfer assignments has only been obliquely discussed in the literature.^{16,19,22} With these assignments as an aid, we assign the absorption and CD spectra of the 2E excited state. In both the ground and excited states, the CD spectra of (Δ) -Cr(bpy) $_3^{3+}$ reveal the positions of transitions not observed in the unpolarized absorption spectra. This is the first report of a comprehensive assignment of both the ground- and excited-state absorption and CD spectra of a molecular species.

Experimental Section

Cr(bpy) $_3(\text{ClO}_4)_3$ was made by a procedure similar to that reported by Baker and Mehta.²⁸ The absorption and emission spectra agree with those previously reported in the literature. The racemic complex was partially resolved by the method of Cartwright et al. using Co(L-cysu) $_3^{3+}$ as the resolving agent.²⁹ After addition of 0.5 equiv of Co(L-cysu) $_3^{3+}$ and filtration, the product in the filtrate was obtained in two fractions by precipitation with $\text{NH}_4(\text{PF}_6)$. The second crop from the filtrate was used in optical experiments, as it was the most optically active (90% Δ isomer). All CD magnitudes reported are corrected and reflect CDs that would be obtained from optically pure samples.^{29,30}

Time-resolved optical density (TROD) spectra were obtained by a standard pump/probe technique. The sample was excited with a 7-ns, 12-mJ pulse at either 266 or 355 nm by a Quanta Ray DCR-1 Nd:YAG laser. The probe beam, generated by a xenon flash lamp, was monitored with a PAR 1420 gated optical multichannel analyzer (OMA), which was gated on for 10 ns beginning 30 ns after the peak of the laser pulse.³¹ The transient absorption was obtained in two spectral regions, from 250 to 400 nm and from 400 to 640 nm. A Corning 0-52 filter ($\lambda(\text{transmission}) > 350$ nm) was placed in the probe beam during the determination of the transient absorption for the 400–640-nm region to prevent light from 200 to 320 nm from emerging through second-order diffraction from the spectrograph. The TRCD spectrum was obtained by a modified pump/probe technique as previously described.¹⁰⁻¹⁴ For TRCD measurements, excitation was with a 355-nm, 12-mJ, 7-ns pulse. The OMA was gated on for 2 μ s starting 1 μ s after the laser pulse. Conventional CD spectra were taken on an Aviv 60DS spectropolarimeter.

In the TROD experiments the solvent was 1 M HCl, as acidic environments decrease the quantum yield of photoaquation of Cr(bpy) $_3^{3+}$.²⁷ For the TRCD experiments the solvent was 10^{-3} M HCl. We observed that (Δ) -Cr(bpy) $_3^{3+}$ photoracemizes, as has been reported for (Δ) -Cr(phen) $_3^{3+}$,^{32,33} and so fresh sample was continuously flowed through the actinic region during the experiment. Solutions were always freshly prepared, deoxygenated by bubbling with argon, and checked after each experiment to make sure no significant amount of photoproduct had formed.

Results

The unpolarized transient absorption difference spectrum and the ground- and excited-state absorption spectra are shown in Figure 1. The magnitude of the transient difference spectrum reflects a correction for incomplete ground-state bleaching (excited-state production), which depends on a knowledge of the portion of the Cr(bpy) $_3^{3+}$ in the probe beam that is excited. Several ways of determining the degree of excited-state production have been applied to the production of the excited state of Ru(bpy) $_3^{2+}$.³⁴⁻³⁷ Since the excited-state spectrum of Ru(bpy) $_3^{2+}$

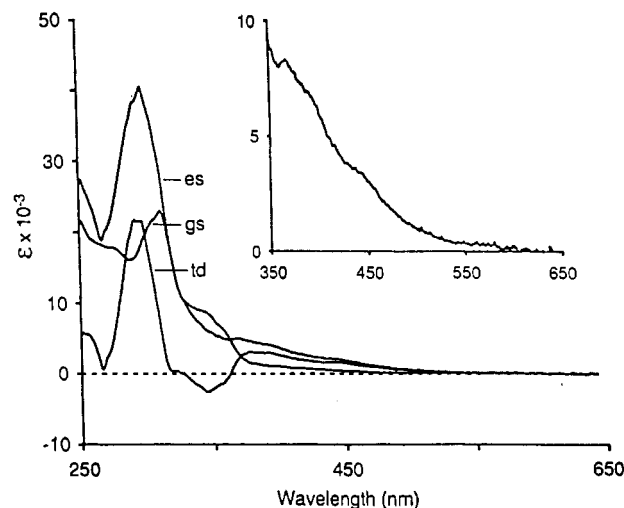


Figure 1. Absorption spectra of Cr(bpy) $_3^{3+}$ in 1 N HCl obtained with the OMA detection system with a 10-ns time gate. The ground-state (gs) and transient difference (td) spectra have been obtained directly and represent 64 averages. Both were taken in two regions, from 250 to 400 nm and from 400 to 640 nm. The transient difference spectrum was obtained 30 ns after excitation with a 7-ns, 266-nm, 12-mJ pulse and is adjusted for the fact that 0.5 of the complex ground state was excited. The 2E excited-state (es) spectrum is the sum of the ground and adjusted transient difference spectra. Inset: Expanded view of the 2E excited-state spectrum from 350 to 640 nm.

is so well studied, we used a method that compares the transient spectrum of Ru(bpy) $_3^{2+}$ and Cr(bpy) $_3^{3+}$ to determine the degree of excitation of the latter. The ground-state bleaching was measured by taking into account that both Cr(bpy) $_3^{3+}$ and Ru(bpy) $_3^{2+}$ have an intersystem-crossing yield of 1.0.^{20,38,39} The degree of ground-state depletion of Ru(bpy) $_3^{2+}$ was determined, and the degree of ground-state depletion was taken to be the same for Cr(bpy) $_3^{3+}$ under identical excitation conditions.⁴⁰ Under our conditions, 50% of the complexes were converted to the excited state. To obtain the actual spectrum of the 2E state, the ground-state spectrum was added to the adjusted transient absorption spectrum. The resulting absorption spectrum for the 2E state is shown in Figure 1.⁴⁰ The above method depends on an accurate knowledge of the extinction coefficients in the transient spectrum of Ru(bpy) $_3^{2+}$. Recently, it has been shown there is probably at least a 10% uncertainty in how well this value can be determined.³⁷ This imprecision is carried over into our calculation of the excited-state absorption of Cr(bpy) $_3^{3+}$ from the ground-state and transient difference spectra. We tested the impact of this on our excited-state spectrum by assuming a $\pm 20\%$ range in the value of the excited-state extinction coefficient of Ru(bpy) $_3^{2+}$ used for estimating the degree of excited-state production. It is clear that though there are changes in the magnitude of the absorption bands, their general character does not change. Excitation of solutions of Cr(bpy) $_3^{3+}$ at 355 nm gives a transient difference spectrum with identical shape.

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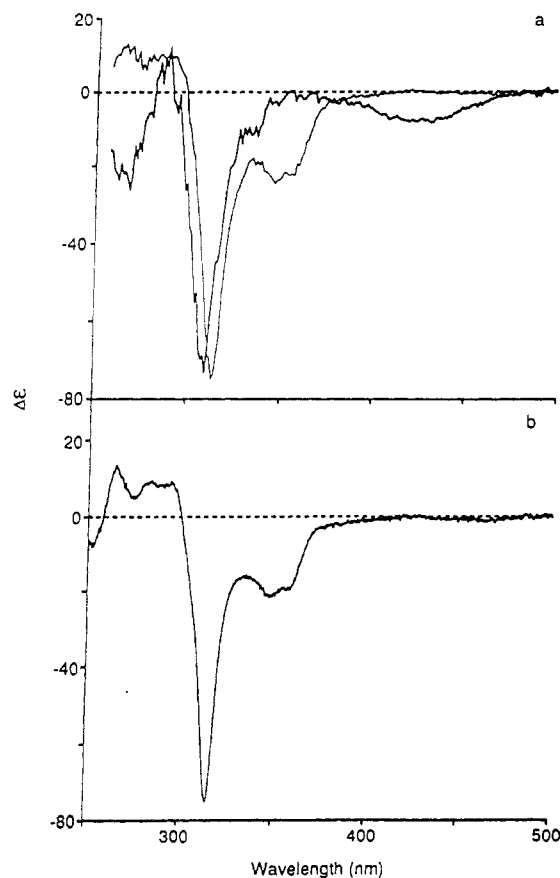


Figure 2. (a) CD spectra of the 4A_2 ground state (thin line) and the 2E excited state (thick line) of $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ in 10^{-3} N HCl taken with the time-resolved CD apparatus. The OMA gate was open for 2 μs starting 1 μs after laser excitation, and 4096 averages were taken. The excited-state spectrum has been corrected for incomplete ground-state depletion (excited-state production) in the manner discussed in the text for the unpolarized excited-state spectrum. The ground-state spectrum was taken under identical conditions except for laser excitation of the sample. (b) CD spectrum of $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ in 1 N HCl obtained on a conventional instrument.

Figure 2a shows the CD spectra of the 2E excited state and of the 4A_2 ground state of $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ taken on the TRCD apparatus. For comparison, Figure 2b shows the ground-state CD spectrum of $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ taken on a conventional instrument. The 2E CD spectrum was corrected for incomplete conversion of the ground state to the excited state in a manner similar to that done for the unpolarized TROD spectrum of $\text{Cr}(\text{bpy})_3^{3+}$. In this case, the unpolarized TROD spectrum of $\text{Cr}(\text{bpy})_3^{3+}$ was obtained under identical excitation conditions, and we found 70% of the complex was converted to the excited state. As discussed above for the calculation of the excited-state absorption spectrum, there is some uncertainty in determining the percent of the $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ that was excited. We found that changing the assumed percent of excitation by as much as $\pm 20\%$ changed the magnitudes of the CDs somewhat, but such changes did not lead to different features in the CD spectrum of the 2E state. The 2E state has a band at 430 nm ($\Delta\epsilon \approx -8$) and a strong bisignate band centered near 299 nm. A negative band centered at 268 nm ($\Delta\epsilon \approx -26$) and a shoulder near 334 nm ($\Delta\epsilon \approx -11$) are also observed.

Discussion

Absorption. It is necessary to understand the ground-state absorption spectrum of $\text{Cr}(\text{bpy})_3^{3+}$ before the excited-state spectrum can be assigned. The only comprehensive assignment of the ground-state absorption spectrum of $\text{Cr}(\text{bpy})_3^{3+}$ has been provided in the detailed work of König and Herzog.⁴² They resolved the solution spectrum into a series of Gaussian components

and assigned all of the visible and UV absorptions to either ligand field or intraligand transitions. However, as has been noted by others, the width and intensity of some of the bands they assign as ligand field transitions actually preclude such an assignment. More recent work has shown that absorptions between 400 and 450 nm originally attributed to ligand field transitions are actually due to transitions composed of singlet-to-triplet intraligand excitations coupled with ${}^4d^3$ metal-centered excitations.^{43,44} There are transitions at 281 and 265 nm ($35\,600$ and $37\,700\text{ cm}^{-1}$) that have extinction coefficients of $16\,300$ and $16\,200$, respectively, as determined by a Gaussian fit of the spectrum.⁴² König and Herzog assigned these as ligand field transitions due to two-electron excitations ($t^3 \rightarrow t^1e^2$). There are also three bands at 359, 346, and 330 nm ($27\,850$, $28\,900$, and $30\,300\text{ cm}^{-1}$) that have extinction coefficients of 5050 , 7200 , and 8100 , respectively. König and Herzog assigned these as due to the ligand field transition ${}^4A_2 \rightarrow {}^4T_1$.³³ However, one would not expect ligand field transitions to have such high intensities, and we suggest that they are all charge-transfer transitions. In fact, suggestions that charge-transfer bands exist in the spectrum of $\text{Cr}(\text{bpy})_3^{3+}$ have occurred in the literature, but specific assignments have not been made.^{16,19,22} Recent work has posited that the charge-transfer region of the spectrum lies above $40\,000\text{ cm}^{-1}$.⁴⁵ We will show below that charge-transfer transitions actually lie at much lower energy.

Positions of LMCT transitions can be estimated by using empirical optical electronegativity calculations.⁴⁶⁻⁴⁸ The following relationship has been developed for LMCT transitions to t_2 orbitals in octahedral complexes: $\nu_{\text{ct}} = 30\,000\text{ cm}^{-1} \times (\chi(\text{L}) - \chi(\text{M})) + \sigma$, where $\chi(\text{L})$ and $\chi(\text{M})$ are empirically determined for each ligand and specific metal oxidation state and σ is the spin-pairing energy. For a transition to an e orbital in an octahedral complex, the octahedral ligand field splitting ($10Dq$) must be added to the transition energy and the spin pairing energy may be different. Lever has compiled χ values for a number of ligands and central metals and has given the functional form for ν_{ct} for different metal configurations.⁴⁸ For Cr(III), $\chi(\text{M}) \approx 1.8$. Lever does not list a value of $\chi(\text{L})$ for bpy, so we have estimated it. $\text{Ru}(\text{bpy})_3^{3+}$ and $\text{Os}(\text{bpy})_3^{3+}$ have LMCT transitions at $14\,790$ and $17\,760\text{ cm}^{-1}$, respectively. $\chi(\text{M})$ is 2.1 and 1.95 for Ru(III) and Os(III) and $\nu_{\text{ct}} \approx 30\,000\text{ cm}^{-1} \times (\chi(\text{L}) - \chi(\text{M})) + (2/3)D$ for a low-spin, d^5 complex. D , which equals approximately $7B$ (B is the Racah parameter), is approximately 3000 cm^{-1} for second- and third-row transition-metal complexes.⁴⁷ From this, $\chi(\text{L})$ for bpy can be estimated to be 2.5. For a d^3 complex, LMCT excitations should lie at approximately $30\,000\text{ cm}^{-1} \times (\chi(\text{L}) - \chi(\text{M})) + 2D$ and $30\,000\text{ cm}^{-1} \times (\chi(\text{L}) - \chi(\text{M})) + 10Dq - 2D$. With $10Dq = 22\,000\text{ cm}^{-1}$ and $D \approx 7B \approx 3500\text{ cm}^{-1}$,⁴⁹ transitions are predicted to be near $28\,000$ and $36\,000\text{ cm}^{-1}$. These are remarkably close to the observed moderately intense transitions at $27\,850$, $28\,900$, and $30\,300\text{ cm}^{-1}$ and at $35\,600$ and $37\,700\text{ cm}^{-1}$. This strongly suggests that the intensity in these absorption bands is due at least in part to LMCT transitions. It is possible that each group of transitions is due to one electronic transition with the splitting due to vibrational effects. Such splittings have been seen in LMCT transitions of $\text{M}(\text{bpy})_3^{3+}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$).⁵⁰

MLCT transitions might also be expected to lie in the observed spectral region. An optical electronegativity relation has been developed for the estimation of the energy of MLCT transitions in d^3 complexes: $\nu_{\text{ct}} \approx 30\,000\text{ cm}^{-1} \times (\chi(\text{M}) - \chi(\text{L})) + (4/3)D$. An estimate of the position of MLCT bands in $\text{Cr}(\text{bpy})_3^{3+}$ can be made by using a comparison with the isoelectronic complex $\text{V}(\text{bpy})_3^{2+}$, which has spin-allowed MLCT transitions as far to

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Table I. Absorption Spectra of the Spin-Allowed Transitions of Cr(bpy)₃³⁺ in the Ground (⁴A₂) and Excited (²E) States^a

wave-number, cm ⁻¹	λ , nm	ϵ	assgnt
Ground State (⁴ A ₂)			
21 440	466	<i>b</i>	⁴ dd (⁴ A ₂ → ⁴ T ₂)
22 000	455	260	} ³ IL ($\pi\pi^*$ \^4,2d)
23 400	427	610	
25 100	398	900	
27 850	359	5050	} ⁴ LMCT ($\pi \rightarrow t_2$)
28 900	346	7200	
30 300	330	8100	
32 050	312	23000	} ¹ IL ($1\pi\pi^*$)
33 400	299	21000	
35 600	281	16300	} ⁴ LMCT ($\pi \rightarrow e$)
37 700	265	16200	
42 150	237	37000	¹ IL ($\pi\pi^*$)
Excited State (² E)			
22 470	445	3800	} ² MLCT ($t_2 \rightarrow \pi(^3\text{Cr(IV)})$)
25 950	385	8000	
33 900	295	41000	¹ IL ($\pi\pi^*$)
39 220	255	28000	² LMCT ($\pi \rightarrow e(^3\text{Cr(II)})$)

^a Experimental ground-state spectral parameters taken from ref 39.^b Estimated position of this transition from ref 61.

the red as 650 nm (15 350 cm⁻¹).⁵¹⁻⁵³ One would expect the equivalent MLCT transition to be at significantly higher energy for a Cr(III) versus a V(II) complex. Unfortunately, the optical electronegativity of V(II) is not reported. However, an estimate of it can be made. The optical electronegativities of Cr(IV), Cr(III), and V(III) are 2.65, 1.8, and 1.9, respectively. If one assumes that the change in the optical electronegativity observed for chromium upon reduction from d² to d³ is followed by vanadium, then V(II) would have an optical electronegativity of about 1.05. This gives an approximate difference for $\chi(M)$ of 0.75 between Cr(III) and V(II). The value of *D* is approximately 3500 cm⁻¹ for Cr(bpy)₃³⁺ and 4550 cm⁻¹ for V(bpy)₃²⁺.^{42,47,48} Thus, MLCT transitions in Cr(bpy)₃³⁺ complexes will lie approximately 21 100 cm⁻¹ higher in energy than in V(bpy)₃²⁺.^{54,55} By analogy to the V(bpy)₃²⁺ spectrum, MLCT transitions in Cr(bpy)₃³⁺ are predicted to occur near 36 450 cm⁻¹ and at higher energies. MLCT transitions thus account for some of the absorption intensity observed in the UV region of the spectrum. However, making specific assignments of the peaks at 281 and 265 nm is not without peril as both LMCT and MLCT transitions should occur in this spectral region and predicting their relative intensities is difficult. We note that all of the charge-transfer transitions observed in the near-UV region must be polarized along the short axis of the ligands, as the long-axis ligand polarized charge-transfer transitions will not be intense.⁵⁸⁻⁶⁰ Table I summarizes the assignment of

the Cr(bpy)₃³⁺ absorption spectrum using assignments made here and elsewhere.

The unpolarized absorption spectrum of the ²E state has been reported from 700 to 350 nm for Cr(bpy)₃³⁺ and other Cr³⁺ tris(imine) complexes.¹⁶ The position of a band at 590 nm was seen to be insensitive to ligand substitution and was attributed to a ligand field transition. We have been unable to reproduce the observation of this absorption band. However, we do see a transient absorption at 590 nm when we do not have a 0-52 filter attenuating the probe beam. This implies that a significant amount of UV light of second order has passed through the spectrograph. The observed transient absorption signal is thus actually due to the transient absorption near 295 nm. Bands were previously observed at 390 and 445 nm in Cr(bpy)₃³⁺. These shifted significantly when the ligand was substituted and were attributed to LMCT transitions.¹⁶ In the excited-state spectrum reported here similar bands are seen. However, they are not as distinct as previously reported, even though our spectral resolution is better (<2 nm) than in the previously reported spectrum (5 nm).

The strong absorption centered near 310 nm in the ground-state spectrum is shifted toward the blue region and is centered near 295 nm in the excited-state spectrum. This transition has been assigned as an exciton-coupled $\pi\pi^*$ intraligand transition in the ground state^{30,42} and is logically given the same assignment in the excited-state spectrum. The intensity of this $\pi\pi^*$ band near 300 nm approximately doubles in the excited-state spectrum. The intensity of this band in the ground state is unusual, as it is significantly smaller in Cr(bpy)₃³⁺ than in the spectrum of other tris(bipyridyl) complexes.⁵⁸ This low intensity for the ¹IL absorption in the ground-state spectrum of Cr(bpy)₃³⁺ may be due to intensity borrowing by nearby charge-transfer transitions.

The position of spin-allowed LMCT bands in the spectrum originating from the ²E state can be estimated by calculating the transition energy of the final state obtained by the optical electronegativity method discussed above. Four orbital promotions are consistent with single-electron, spin-allowed excitations: ²(t₂³) → ²(πt_2^4) and ²($\pi t_2^3 e$), with the metal having either a singlet or triplet spin configuration for each of the orbital configurations. The calculated energies obtained are $\chi - D$, $\chi + D$, $\chi + 10Dq - D$, and $\chi + 10Dq + D$ for the πt_2^4 (³Cr(II) and ¹Cr(II)) and $\pi t_2^3 e$ (³Cr(II) and ¹Cr(II)) spin-allowed transitions from ²E, respectively (here, $\chi = 30\,000\text{ cm}^{-1} \times (\chi(L) - \chi(M))$). From values stated above for χ , *D*, and 10*Dq*, LMCT transitions are predicted at 17 500, 24 500, 39 500, and 46 500 cm⁻¹. The observed transitions at 445 and 385 nm (22 500 and 25 970 cm⁻¹) lie near the predicted position of the πt_2^4 (¹Cr(II)) transitions, and they can be assigned as due, at least in part, to such transitions. There is a band at 255 nm (39 220 cm⁻¹), and this may be assigned as due at least in part to an LMCT transitions involving $\pi t_2^3 e$ (³Cr(II)). Transitions due to πt_2^4 (³Cr(II)) absorption, predicted to lie near 17 500 cm⁻¹, are not observed. This may be due to their having weak intensity and thus being obscured by the tail of the absorption band at 445 nm.

The excited-state bands observed at 445 and 385 nm may also be assigned as partly due to MLCT transitions. As discussed above, MLCT bands are expected to lie near and above 36 450 cm⁻¹ in the ground-state spectrum. Spin pairing considerations imply that the energy of some MLCT transitions should be significantly lower in the ²E spectrum. In the transfer of an electron from the metal to a ligand, the lowest energy MLCT states produced from both the ground and ²E state will have two unpaired electrons on the metal (³Cr(IV)). The difference between the two MLCT states reached is the relative spin orientation of the unpaired electron on the ligand(s) to the spin orientation of the unpaired electrons on the metal. The exchange energy between an unpaired ligand electron and a metal electron is not considered to be large due to the low coincidence of their orbitals.⁴⁷ Thus, the energies at which equivalent ⁴MLCT and ²MLCT states lie

(51) König, E.; Herzog, S. J. *Inorg. Nucl. Chem.* **1970**, *32*, 601.(52) Maverick, A. W.; Shah, S. S.; Kiraier, C.; Holton, D. *Inorg. Chem.* **1987**, *26*, 774.(53) Estimation of the position of charge-transfer bands by correlation with their position in similar complexes of different metals is a time-tested method. A recent example is the assignment of an LMCT transition in Co(CN)₆³⁻: Miskowski, V. M.; Gray, H. B. *Comments Inorg. Chem.* **1985**, *4*, 323.(54) Calculated from $\Delta E_{\text{MLCT}}(\text{Cr(III)} - \text{V(II)}) = 30\,000\text{ cm}^{-1} \times (\chi(\text{Cr(III)}) - \chi(\text{V(II)}) + (4/3)(D(\text{Cr(III)}) - D(\text{V(II)})))$.(55) It may seem that the placement of MLCT transitions in Cr(bpy)₃³⁺ at such a low energy is untenable, as the ground-state complex cannot be oxidized to Cr(bpy)₃⁴⁺. However, the oxidation potential of V(bpy)₃²⁺ is -0.5 V (vs Ag⁺/AgCl⁵⁶), and so the 2.6 eV higher MLCT energy for Cr(bpy)₃³⁺ would imply that its ground-state oxidation potential is near -3.1 V (vs Ag⁺/AgCl). This is consistent with the absence of Cr(bpy)₃⁴⁺. We note that the ²E state of Cr(bpy)₃³⁺ is readily oxidatively quenched by Fe(CN)₆³⁻,⁵⁷ a result that is also consistent with our assignment of MLCT transitions in the spectrum.(56) Shah, S. S.; Maverick, A. W. *Inorg. Chem.* **1986**, *25*, 1867.(57) Juris, A.; Manfrin, M. F.; Maestri, M.; Serpone, N. *Inorg. Chem.* **1978**, *17*, 2258.(58) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. A* **1969**, 1428.(59) Day, P.; Sanders, N. *J. Chem. Soc. A* **1967**, 1536.(60) Orgel, L. E. *J. Chem. Soc.* **1961**, 3683.(61) Josephsen, J.; Schaffer, C. E. *Acta Chem. Scand.* **1977**, *A31*, 813.

above the ground state should be very similar. Since the 2E state is $13\,700\text{ cm}^{-1}$ above the ground state,^{16,24} MLCT transitions should occur at an energy approximately this much lower in energy in the 2E spectrum. If one assumes that the excited-state absorption bands at 445 and 385 nm are MLCT, one predicts that there should be MLCT transitions in the ground-state spectrum (4A_2) near 276 and 252 nm ($36\,230$ and $39\,680\text{ cm}^{-1}$). Charge-transfer transitions are seen in the ground-state spectrum at 281 and 265 nm, and as discussed above, these may be at least partly due to MLCT transitions. Thus, ground- and excited-state spectra are consistent with a tentative assignment of the transitions at 445 and 385 nm in the 2E spectrum as a mixture of LMCT and MLCT. This is in contrast to a previous assignment of these bands in the excited-state spectrum as due solely to LMCT transitions.¹⁶ Table I compiles the current assignment of the excited-state (2E) spectrum.

Circular Dichroism. The CD spectrum of the ground state of resolved $\text{Cr}(\text{bpy})_3^{3+}$ has been previously reported.³⁰ The only bands in the spectrum that have been assigned are those due to the ${}^1IL\ \pi\pi^*$ transitions. For tris(bipyridyl) complexes the absolute value of the magnitude of these transitions is greater than 50 and it usually dominates the CD spectrum near 300 nm. It is clear that the negative band at 313 nm ($\Delta\epsilon \approx -75$) and part of the positive bands below 300 nm (295 nm, $\Delta\epsilon \approx 9.5$) are due to the exciton coupling between the ${}^1\pi\pi^*$ transitions on the bpy ligands.

This leaves CD bands at 460 nm ($\Delta\epsilon \approx -1.2$), 356 nm ($\Delta\epsilon \approx -19.5$), and 347 nm ($\Delta\epsilon \approx -20$) and a series between 300 and 250 nm (e.g. 264 nm, $\Delta\epsilon \approx 12$, 280 nm, $\Delta\epsilon \approx 9$) as unassigned. The weak CD at 460 nm lies near both the ${}^4A_2 \rightarrow {}^4T_2$ and the lowest energy ${}^3\pi\pi^*$ transitions (Table I). As both are expected to have weak CDs, we assign this band to the sum of these two transitions.^{28,61} The moderately intense CDs at 356 and 347 and between 250 and 300 nm lie in spectral regions where charge-transfer transitions are expected to lie. Charge-transfer transitions gain CD intensity by a variety of mechanisms. Ligand long-axis-polarized MLCT and LMCT transitions can gain intensity via borrowing mechanisms from the intense CD 1IL transitions.⁵⁸ As the charge-transfer transitions that have significant intensity in absorption are polarized along the short axis of the ligands, the charge-transfer transitions that gain CD intensity by this mechanism will be transitions different from the charge-transfer bands seen in the absorption spectrum. Another mechanism by which a charge-transfer transition can gain CD intensity is by coupling with d-d transitions. In this case the charge-transfer transition may gain a significant magnetic transition moment and from this a significant rotational strength.⁶² Whatever the mechanism by which the charge-transfer transitions gain CD intensity, the CD bands at 356 and 347 nm must be due to LMCT transitions. As discussed above, LMCT transitions are expected in this region of the spectrum, while MLCT transitions only occur at higher energies. For the CDs between 300 and 250 nm, both LMCT and MLCT transitions may contribute. The weak positive lobe of the ${}^1IL\ \pi\pi^*$ exciton-coupled CD will also be in this region of the spectrum, probably comprising the bulk of the band at 295 nm ($\Delta\epsilon \approx 9.5$). Table II summarizes the assignments of the CD spectrum of $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ made here and elsewhere.

The CD of the 2E absorption has a bisignate band with extrema at 310 nm ($\Delta\epsilon \approx -69$) and 288 nm ($\Delta\epsilon \approx 12$). This CD is clearly due to the exciton-coupled intraligand ${}^1\pi\pi^*$ transitions. It has been previously shown that the magnitude of the CD of the long-axis $\pi\pi^*$ absorption in imine complexes depends strongly on the number of ligands whose transitions participate in the exciton coupling.^{3,62,63} In the case of tris complexes the absolute value of the magnitude of $\Delta\epsilon$ is greater than 50. For bis(imine) complexes the magnitude varies from 20 to 100, depending on the metal, its oxidation state, and the ligand. However, for a bis complex the value of $\Delta\epsilon$ is always found to be much smaller than for the equivalent tris complex. In the current case, the 2E long-axis-polarized $\pi\pi^*$ CD is nearly the same magnitude as the

Table II. Circular Dichroism Spectra of the Spin-Allowed Transitions of $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ in the Ground (4A_2) and Excited (2E) States^a

λ , nm	$\Delta\epsilon$	assignt
Ground State (4A_2)		
460	-1.2	$\left\{ \begin{array}{l} {}^3IL\ (\pi\pi^*, {}^4,2d) \\ {}^4dd\ ({}^4A_2 \rightarrow {}^4T_2) \end{array} \right.$
356	-19.5	$\left\{ \begin{array}{l} {}^4LMCT\ (\pi \rightarrow t_2) \end{array} \right.$
347	-21	
315	-75	
295	9.5	$\left\{ \begin{array}{l} {}^1IL\ (\pi\pi^*) \end{array} \right.$
280	9	$\left\{ \begin{array}{l} {}^4LMCT\ (\pi \rightarrow e) \\ {}^4MLCT\ (t_2 \rightarrow \pi) \end{array} \right.$
264	12	
Excited State (2E)		
430	-8	$\left\{ \begin{array}{l} {}^2MLCT\ (t_2 \rightarrow \pi({}^3\text{Cr}(\text{IV}))) \\ {}^2LMCT\ (\pi \rightarrow t_2({}^1\text{Cr}(\text{II}))) \end{array} \right.$
334	-11	
310	-69	$\left\{ \begin{array}{l} {}^1IL\ (\pi\pi^*) \end{array} \right.$
288	12	$\left\{ \begin{array}{l} {}^2LMCT\ (\pi \rightarrow e_g({}^3\text{Cr}(\text{II}))) \end{array} \right.$
268	-26	

^a Ground-state CD magnitudes are taken from the conventional CD spectra. Excited-state CD magnitudes are taken from TRCD spectrum corrected to total excited-state production.

analogous ground-state CD, implying that there is about the same exciton coupling in these transitions emanating from the 4A_2 and 2E states. This is as expected, since the primary difference between the two states is a spin flip in an electron associated with the metal orbitals. Such a difference would not be expected to strongly influence the interaction of intraligand transition dipoles. Similar small changes in the relative magnitude of the CD in the $\pi\pi^*$ band in the excited-state absorption was seen for $(\Delta)\text{-Fe}(\text{bpy})_2^{2+}$, whose lowest excited state is also metal centered.¹⁵ In contrast, for the same $\pi\pi^*$ transition in $(\Delta)\text{-Ru}(\text{bpy})_3^{2+}$ there is a significant decrease in the magnitude of the CD in the 3MLCT excited state spectrum due to the single-ligand localization of the electron transferred from the metal to the ligands.^{12,13} Thus, in $(\Delta)\text{-Ru}(\text{bpy})_3^{2+}$ one ligand becomes reduced and significant coupling in the long-axis $\pi\pi^*$ transition only occurs between the two unreduced ligands.

In the CD spectrum of the 2E state there are three other observed bands. One is broad and centered at 430 nm with $\Delta\epsilon \approx -8$. A charge-transfer assignment seems consistent, as the magnitude of this CD is similar to the magnitude of the CDs of charge-transfer transitions in the ground-state spectrum. As discussed above for the absorption spectrum of the 2E state, both LMCT and MLCT transitions are expected in this spectral region, and so the 430-nm CD band may be assigned to CD intensity from the sum of both types of transitions. This CD lies about 15 nm to the blue side of the peak of the closest absorption band observed in the excited-state absorption spectrum, and it is probably due to transitions different from those seen in the absorption spectrum. The CD observed at 334 nm ($\Delta\epsilon \approx -11$) in the 2E spectrum does not have a corresponding transition in the excited-state absorption spectrum. It is due to either an LMCT or MLCT transition that has a much stronger CD intensity than absorption intensity. The CD band centered at 268 nm ($\Delta\epsilon \approx -26$) in the 2E spectrum is similar in magnitude to the CDs in the ground-state CD spectrum that are assigned as charge-transfer transitions. As discussed above for the excited-state absorption spectrum, LMCT transitions are expected in this region of the 2E spectrum, and so an LMCT assignment is reasonable. In this region of the spectrum the position of the bands assigned as 2LMCT in the absorption and CD differ by 13 nm, and so it appears that they are due to different 2LMCT transitions.

The current study illustrates that TRCD can be useful in revealing the position of excited-state transitions not seen in unpolarized excited-state absorption. This is not surprising, as the selection rules that govern intensity in absorption and CD differ, and thus the features in their respective excited-state spectra might be expected to differ. For the 2E excited state of $(\Delta)\text{-Cr}(\text{bpy})_3^{3+}$ the observed absorption and CD charge-transfer bands appear to be due to different transitions. That different transitions are

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intense in the CD and absorption spectra of an excited state has also been observed in the spectra of the excited triplet state of 4-thiouridine in tRNA.⁶⁴ The current work is the first comprehensive assignment of both the absorption and CD spectra of

both the ground- and metastable excited-states of a molecular complex.

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Low-Temperature Precursor Synthesis of Crystalline Nickel Disulfide

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Pure, crystalline nickel disulfide is synthesized within seconds from the solid-state reaction between potassium hexafluoronickelate(IV) and sodium pentasulfide hydrate at ~65 °C. The nickel disulfide product is isolated by simply washing away the byproduct salts. The reaction is influenced by the hydration and the sulfur content of the sulfiding agent and by the transition-metal precursor. Increasing the hydration of the sodium pentasulfide or lowering the oxidation state of the nickel in potassium hexafluoronickelate from Ni(IV) to Ni(III) favors a less crystalline product. Reactions containing sulfiding agents with lower sulfur content, such as sodium monosulfide or sodium disulfide, produce mixtures of nickel monosulfide and nickel disulfide. X-ray diffraction, thermogravimetric analysis, and differential scanning calorimetry results are presented.

Introduction

Crystalline transition-metal chalcogenides have traditionally been synthesized by reacting stoichiometric amounts of their constituent elements in evacuated silica tubes at 500–1200 °C.^{1,2} Intermittent grinding and reheating are often necessary to obtain a pure phase. Precursor syntheses are important for providing lower temperature pathways and often more rapid methods of preparing known materials. Occasionally, new kinetically stable phases are discovered.³ Some low-temperature precursor routes to group IV–VI transition-metal sulfides are known. These include metathesis reactions between transition-metal halides and alkali-metal sulfides carried out in nonaqueous solvents⁴ or reactions between transition-metal halides and covalent sulfiding agents such as silyl sulfides.^{5–7} Solution reactions generally produce finely divided materials that become crystalline only after annealing at elevated temperatures. Thermal decomposition of the precursors ammonium thiomolybdate and ammonium thiotungstate yields several molybdenum and tungsten sulfide phases.^{8,9} In addition, thin films of some group VI and VIII transition-metal dichalcogenides can be prepared by reacting transition-metal carbonyls with a sulfur source.^{10,11}

Low-temperature routes to group VIII transition-metal sulfides are not as well explored. Reactions between anhydrous hexachlorometalates(IV) and hydrogen sulfide at 110–250 °C produce poorly crystallized transition-metal dichalcogenides.^{12,13} Anhydrous transition-metal chlorides react with ammonium hydrogen sulfide in polar organic solvents at room temperature.¹⁴ The

products of these reactions are amorphous materials. When anhydrous transition-metal sulfates are exposed to a mixture of hydrogen and hydrogen sulfide at 325–525 °C, metal-rich sulfides are formed.¹⁵

Delafosse and Barret prepared nickel disulfide from nickel sulfate and hydrogen sulfide at 230 °C.¹⁶ Subsequent experiments by Bouchard, however, suggest that the products of this reaction are poorly crystallized, contain small amounts of water, and are extremely reactive toward oxidation in air.¹⁷ Another route to nickel disulfide involves heating nickel monosulfide with excess sulfur. This reaction reportedly occurs at temperatures as low as 170 °C over a period of 40 h.¹⁸ Our experience, however, has demonstrated that the starting materials must be very finely divided. If they are not, much higher temperatures (≥450 °C) are required in order to obtain a pure, crystalline phase. Nickel metal and excess sulfur react at about 500 °C to produce nickel disulfide. Repeated grinding and firing with excess sulfur is needed to get a pure, single-phase material.¹⁹

We report here a quick, high-yield method for the preparation of crystalline nickel disulfide via a solid-state reaction that is initiated at low temperature. The synthetic method involves the reaction of a high-oxidation-state nickel fluoride complex with an alkali-metal sulfiding agent. The best precursors found are potassium hexafluoronickelate(IV) and sodium pentasulfide hydrate. This approach to the rapid low-temperature synthesis of nickel disulfide represents a model study for solid-state precursor syntheses that could be applicable to many other transition-metal chalcogenides.

Experimental Section

Potassium hexafluoronickelate(IV), K₂NiF₆, was prepared by reacting a 2:1 mixture of potassium chloride and anhydrous nickel chloride (Alfa, ultrapure) with excess fluorine gas (98%, Spectra Gases) at 275 °C for approximately 6 h.²⁰ High-grade stainless-steel tubes were passivated with fluorine prior to loading the salts. All transfers of reagents and precursors were carried out in a He-filled drybox (Vacuum Atmo-

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