1986 Inorganic Chemistry, Vol. 12, No. 9, 1973

Contribution from the Institut fur Physikalische Chemie,
Universitat Frankfurt, Frankfurt, Germany

Luminescence Spectrum of Bis(2,6-pyridinedicarboxylato)chromate(III)

P. E. HOGGARD* and H.-H. SCHMIDTKE

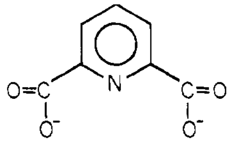
Received December 8, 1972

The luminescence spectrum of sodium bis(2,6-pyridinedicarboxylato)chromate(III) has been measured and the fine structure attributed to vibrational coupling. The presence of vibrational modes in the phosphorescence spectrum has been used as an indicator of metal atom participation in these modes. The absence of a "pseudo-Stokes shift" was explained in terms of an emission from a derivative state of the octahedral ^2E_g level.

Introduction

In a previous paper the luminescence spectra of chromium(III) complexes with iminodiacetic acid, H_2IDA=N-$(CH_2COOH)_2$, and methyliminodiacetic acid, H_2MIDA=$(CH_3)N(CH_2COOH)_2$, were reported.[1] The fine structure in the phosphorescence spectrum of the *trans(fac)*-$[Cr(MIDA)_2]^-$ complex was attributed to vibrational coupling, and the concept of a pseudo-Stokes shift was introduced to explain the absence of any detectable emission at all in the neighborhood of (and including) the O–O line, which itself had to be determined by comparison of reflectance and emission spectra. This complex emitted in the region from 600 to 3000 cm^{-1}, measured from O–O position, and the "hole" between 0 and 600 cm^{-1} was ascribed to the effects of a shifted excited state potential surface, *i.e.*, a pseudo-Stokes shift analogous to the Stokes shift observed with continuous curves.

In this paper we examine the phosphorescence spectrum of an analogous complex, bis(2,6-pyridinedicarboxylato)chromate(III). The pyridinedicarboxylate ligand (PDC) has the same backbone as IDA and MIDA, but is held more rigidly in place by the pyridine ring system.



PDC

We have also made an attempt to establish a closer relationship between fine structure in the phosphorescence spectrum and the vibrational levels of the system, including those levels which show up in Raman spectra.

Experimental Section

The complex $K[Cr(MIDA)_2]$ was prepared as previously described.[2] $NH_4[Cr(PDC)_2]$ has been reported by Hartkamp.[3] For the preparation of the $Na[Cr(PDC)_2]\cdot1.5H_2O$ complex used in this work, essentially the same procedure was used as for $K[Cr(MIDA)_2]$. $Cr(NO_3)_3\cdot9H_2O$ (10.0 g, 0.025 mol) was dissolved in 50 ml of warm H_2O. Likewise 8.4 g of H_2PDC (0.05 mol) and 4.0 g of NaOH (0.1 mol) were dissolved in an equal amount of warm water, and this solution then was added slowly to the chromium solution. The reaction mixture was heated for 2 hr at 90° and allowed to cool, whereupon a crystalline violet precipitate was formed. This was collected and recrystallized from water, yield 6.5 g (60%). *Anal.* Calcd for $Na[Cr(PDC)_2]\cdot1.5H_2O$: Cr, 12.05; C, 38.9; H, 2.09; N, 6.50. Found: Cr, 12.2; C, 38.95, 38.74; H, 2.16, 2.35; N, 6.38.

Luminescence spectra were obtained with a previously described apparatus,[4] utilizing a Spex 1700-II 0.75-m Czerny-Turner grating monochromator. Spectra were taken on powdered samples, usually at 85°K, and were read out on a strip-chart recorder. The scan rate was 20–40 Å/min. Spectra were recorded several times and at various sensitivities.

Reflectance spectra at 100°K were obtained with a Cary Model 14 spectrophotometer together with a Cary three-port illuminator attachment. Spectra were recorded on pellets fixed onto a brass holder, which was immersed in a dewar through which boiling N_2 gas was circulated. Details of this direct reflectance method have been given elsewhere.[5] A Cary diffuse reflectance attachment was used for reflectance spectra at room temperature. Laser Raman spectra were recorded with a Cary Model 82 spectrometer, using the (150 mW) 6471-Å line of a krypton laser. Infrared spectra were recorded with a Perkin-Elmer Model 421 spectrometer.

Results

The emission spectrum of $Na[Cr(PDC)_2]\cdot1.5H_2O$ at 85°K in powder form is typical for phosphorescence spectra of chromium(III) complexes from a doublet excited state, exhibiting several narrow lines with half-widths near 20 cm^{-1}. A strong line, representing presumably the zero phonon transition, was observed at 7852 Å, and a series of lines with generally decreasing intensity was observed on the low-energy side out to 1100 cm^{-1} from the O–O line. The line positions and relative intensities are listed in Table I and the phosphorescence spectrum is shown in Figure 1. The spectrum was independent of the excitation wavelength used.

The diffuse reflectance spectrum at room temperature was featureless in the intercombination band region, whereas the direct reflectance spectrum taken at 100°K exhibited a few weak lines. Because the resolution with this technique is not very good in comparison with that for emission spectra, the peaks could not be located with an accuracy greater than ±30 cm^{-1}, and half-widths were typically around 100 cm^{-1}. A relatively intense line was observed at 783 mμ, confirming the assignment of the 7852-Å line in the phosphorescence spectrum to the O–O transition. The rest of the observed peaks lay at higher energies, as expected for vibrational satellites.

The intercombination band reflectance data are listed in Table II. The energies of the vibrational levels of the (octahedral) ^2E_g excited state inferred from the reflectance spectrum correlate fairly well with values found in the phosphorescence spectrum, applying to ground state vibrational levels, which indicates some similarity between the shapes of the potential surfaces in ground and excited states.

Infrared spectra were recorded down to 250 cm^{-1} for $Na[Cr(PDC)_2]\cdot1.5H_2O$, as well as for H_2PDC and H_2MIDA, and are tabulated together with that of $K[Cr(MIDA)_2]^1$ in Table III, for the region 250–1100 cm^{-1} appropriate to analysis of the phosphorescence spectra.

---

* Correspondence to this author should be addressed to the Department of Chemistry, University of British Columbia, Vancouver 8, Canada.

[1] P. E. Hoggard and H.-H. Schmidtke, *Ber. Bunsenges. Phys. Chem.*, 76, 1013 (1972).

[2] J. A. Weyh and R. E. Hamm, *Inorg. Chem.*, 7, 2431 (1968).

[3] H. Hartkamp, *Z. Anal. Chem.*, 187, 16 (1962).

[4] H. Gausmann and H. L. Schlafer, *J. Chem. Phys.*, 48, 4056 (1968).

[5] (a) W. Geis, Dissertation, Frankfurt am Main, 1971; (b) G. Herzog, unpublished results.

Table I. Luminescence Data for Na[Cr(PDC)$_2$]·1.5H$_2$O, 85°K

$\bar{\nu}$, cm^{-1}	Intensity[a]	Half-width,[b] cm^{-1}	12,736 − $\bar{\nu}$, cm^{-1}
12,898	1	38	−162
12,736	100	30	0
12,697	2		39
12,649	1		87
12,523	20	23	213
12,492	1		244
12,413	2	18	323
12,376	0.5	18	360
12,312	2	30	424
(12,270)	<0.1		(466)
12,183	5	19	553
(12,100)	<0.1		(636)
12,058	0.1		678
11,973	0.4	50	763
11,889	0.05		847
11,839	0.08		897
11,754	0.05		982
11,640	0.08		1096

[a] Relative to O–O line = 100. [b] With 0.8-mm slit width.

Table II. Reflectance Data for Na[Cr(PDC)$_2$]·1.5H$_2$O, 100°K

λ, mμ	$\bar{\nu}$, cm^{-1}	Intensity[a]	$\bar{\nu}$ − 12,736
783	12,770	1	−34
775	12,900	1	160
767	13,040	0.1	300
752	13,300	0.1	560
741	13,500	0.1	760

[a] Relative to O–O line = 1.

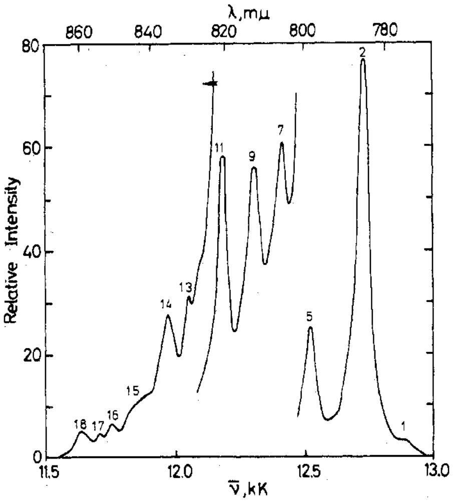


Figure 1. Luminescence spectrum of Na[Cr(PDC)$_2$]·1.5H$_2$O at 85°K.

In addition, laser Raman spectra were recorded for the complexes Na[Cr(PDC)$_2$]·1.5H$_2$O and K[Cr(MIDA)$_2$] and are listed in Table IV. The hot-band luminescence spectrum interfered with the Raman spectrum of K[Cr(MIDA)$_2$] above 400 cm^{-1}, but for both complexes there were very few lines observable above 200 cm^{-1} anyway.

Discussion

1. Characterization of the Complex. It can be seen from molecular models that PDC can coordinate in only one way, assuming it is functioning as a tridentate ligand, namely, meridionally, and therefore only one isomer is possible, *trans*(*mer*)-[Cr(PDC)$_2$]$^-$. The asymmetric carboxylate stretching frequency lies at 1655 cm^{-1} in the complex, typical for coordinated carboxylate groups, and at 1685 cm^{-1} in the free acid. Both the sharpness and the position of the carboxylate stretching band in the complex support the assumption of four equivalent, coordinated carboxylate groups.

Unlike *trans*(*fac*)-[Cr(MIDA)$_2$], the PDC complex has no possible molecular inversion center. Assuming the carbonyl groups, which each have two possible orientations, are optimally positioned, the molecular symmetry group is D_2.

2. Assignment of Fine Structure. Under strict D_2 symmetry infrared absorption is allowed for vibrations with B$_1$, B$_2$, and B$_3$ symmetry, while all vibrations (A, B$_1$, B$_2$, B$_3$) are allowed in the Raman effect. The phosphorescence emission,[6] $^2A \rightarrow {}^4B$, can borrow intensity, through spin-orbit coupling, from all components of the octahedral $^4T_{2g} \rightarrow {}^4A_{2g}$ transition, as well as from two components of the $^4T_{1g} \rightarrow {}^4A_{2g}$ transition. All vibrations become active through this mechanism. This would imply that all coupled fundamental vibrational modes should also be found in Raman and infrared spectra, if not in Raman spectra alone.

The infrared and Raman spectra, however, do not exhibit coinciding bands (although a comparison in the region below 250 cm^{-1} was not possible), nor is the first quartet-quartet transition extraordinarily intense in absorption (ϵ ~200), although in D_2 it is symmetry allowed, and so there probably exists a partially effective center of symmetry. The noncoincidence of ir and Raman bands is also partially accountable in that vibrational modes with A symmetry are the most intense in Raman spectra.[7] There was not a large number of peaks in our Raman spectra, and it may be that most of them represented vibrations of A symmetry which are excluded from ir spectra.

Insofar as a center of symmetry is effective, vibrations can be classified as even and odd, possibly active in Raman and infrared or electronic spectra, respectively. In assigning the observed frequencies in the luminescence spectra we have attempted to maintain this even-odd classification wherever possible, whereby observed levels must correspond to observed infrared frequencies, odd multiples thereof, or combinations of an ir frequency with one or two Raman frequencies, *i.e.*, "odd" fundamentals with their even overtones or combinations of an "odd" with one or more "even" modes.

In the harmonic oscillator approximation vibrational transitions to overtone and combination levels are forbidden, but this selection rule does not apply when the transitions originate from another electronic potential surface, and overtone and combination bands are actually quite prominent in some chromium(III) phosphorescence spectra.[1]

Using the above principles as guidelines it is possible to analyze the fine structure in phosphorescence spectra to a large extent. Table V illustrates such a correlation for Na[Cr(PDC)$_2$]·1.5H$_2$O and for K[Cr(MIDA)$_2$] in the same region. The even-odd classification could not be maintained throughout but was useful as a reference point, especially since CrN$_2$O$_4$ skeletal modes, for which a center of symmetry is most likely to apply, are thought to be electronically the most strongly coupled vibrations. Interestingly enough, the even-odd classification was more effective for K[Cr(MIDA)$_2$] which probably has a true molecular symmetry center.

These correlations are not unique, but they involve only a relatively small number of fundamental frequencies with a large amount of repetition. The argreement is generally good, and several analogous features appear in the assignments for both complexes. We therefore feel that the correlations are for the most part plausible.

Several factors can contribute to the appearance of fine structure in Cr(III) phosphorescence spectra, including coupling with the vibrational levels of the ground state, splitting of the excited state through spin-orbit coupling,

---

(6) J. R. Perumareddi, *Coord. Chem. Rev.*, 4, 73 (1969).

(7) G. Herzberg, "Infrared and Raman Spectra," Van Nostrand, Princeton, N. J., 1945, p 337.

Table III. Infrared Data[a]

$Ni(py)_4Br_2$[b]	Pyridine[b]	H_2PDC	$Na[Cr(PDC)_2]\cdot1.5H_2O$	H_2MIDA	$K[Cr(MIDA)_2]$
			361 w	338 vw	300 vw
427	403	416 vw	443 s	364 s	351 w
		507 vwb	527 vwb	390 vw	404 w
		577 vwb	581 vw	437 vw	416 vw
624	601	647 w	676 w	451 s	430 vs
703, 698	700	700 vs	694 vw	480 s	474 s
			744 s	544 s	522 s
773, 767	747	751 s	774 s	568 vw	604 vw
		852 vw	847 vw	586 s	572 w
		916 vwb	914 w	676 s, 692 vw	740 vs
1008	991	994 w			
1040	1031				
1073	1067	1079 vw	1087 s	879 s, 901 w	894 w, 916 vs, 931 vw
				954 w	960 vw, 978 w
				1012 w	1008 s
				1050 w	1091 s

[a] Peaks for $Na[Cr(PDC)_2]$ are correlated with those for H_2PDC, pyridine, and $Ni(py)_4Br_2$. Peaks for $K[Cr(MIDA)_2]$ are correlated with those for H_2MIDA. Range 250–1100 cm^{-1}. [b] Data from ref 14: b = broad, vs = very strong, s = strong, w = weak, vw = very weak.

Table IV. Raman Data for $Na[Cr(PDC)_2]\cdot1.5H_2O$ and $K[Cr(MIDA)_2]$

Raman shift, cm^{-1}	
$Na[Cr(PDC)_2]\cdot1.5H_2O$[a]	$K[Cr(MIDA)_2]$[a]
32 (17)	38 (2)
40 (6)	60 (4)
59 (4)	74 (2)
90 (5)	92 (5)
113 (15)	107 (15)
354 (1)	200 (15)
419 (2)	211 (1)
453 (2)	221 (1)
	480 (2)

[a] Relative intensities in parentheses.

Jahn-Teller effects, and lower symmetry, and splitting of the ground state, so-called Davydov splitting, through Cr-Cr interaction inside the unit cell. Splitting is also seen as a result of different luminescent sites in the crystal.[8]

Splittings of the ^2E_g state have been observed on the order of 50 cm^{-1} in octahedral complexes in crystal sites of lower symmetry[9,10] and as high as 200 cm^{-1} in some pentaamminechromium(III) complexes.[11] On the other hand, in $[Cr(NH_3)_6](ClO_4)_3$, where the Cr atom is situated in an octahedral crystal site, no splitting has been observed.[12]

In spite of the fact that two O-O lines are to be expected from a splitting of the ^2E_g level of perhaps 200 cm^{-1}, no such splitting was found in $Na[Cr(PDC)_2]\cdot1.5H_2O$, and repeating elements of, for example, 32, 113, and 213 cm^{-1} could be explained satisfactorily in terms of vibrational coupling. The same applies to the $K[Cr(MIDA)_2]$ complex.

In particular, the strong coupling to a 213-cm^{-1} frequency in $Na[Cr(PDC)_2]\cdot1.5H_2O$, as well as the inferred coupling to the same frequency in $K[Cr(MIDA)_2]$,[1] leads us to predict that a 213-cm^{-1} line also appears in the infrared spectrum.

3. Origin of Vibronic Coupling. We now wish to consider the problem of which type of vibration is coupled to the electronic transitions $^2E_g \rightarrow {}^4A_{2g}$ (in octahedral notation). It is natural to assume that those vibrations interact the strongest which involve the Cr atom directly. Indeed, Flint and Greenough[12] find in the case of $[Cr(NH_3)_6](ClO_4)_3$ that all odd CrN_6 skeletal vibrations and Cr-N-H bending vibrations appear in the phosphorescence spectrum, as well as two even skeletal vibrations, usually as combinations with odd vibrations. Other directly coupled single vibrational modes are generally of t_{1u} symmetry.

In the PDC complex a 213-cm^{-1} vibration appears to play a dominant role, occurring strongly coupled by itself, in overtones, and in combination bands. Since exactly the same frequency is found in the phosphorescence of the MIDA complex, it would seem likely that this represents a Cr-O stretching frequency. In metal-glycine complexes, however, Condrate and Nakamoto have assigned a band occurring consistently around 210 cm^{-1} to a ring deformation mode, involving primarily N-Cr-O bending, with the Cr-O stretching contributing to two vibrations with frequencies 100-250 cm^{-1} higher.[13] Flint and Greenough have also noted that bending modes which include the metal atom are coupled more strongly than metal-ligand stretching modes in $[Cr(NH_3)_6](ClO_4)_3$.[12] Nevertheless, it seems unlikely that such a mode would remain unaffected by substitution of pyridine for the $-CH_2-N(CH_3)-CH_2-$ section of the ligand backbone, and, therefore, the assignment of the Cr-O stretching frequency to the 213-cm^{-1} component should not be entirely ruled out.

The infrared spectrum of $Na[Cr(PDC)_2]\cdot1.5H_2O$ in the region from 250 to 1100 cm^{-1} shows roughly the same number of bands as the free acid H_2PDC. It is possible to correlate the peaks in the two spectra with a reasonable degree of confidence merely by visual comparison. An additional aid is provided by considering the pyridine portion alone. The infrared bands for pyridine in the same region[14] are easily matched up with the corresponding bands in H_2PDC. Gill, *et al.*, have studied the shifts of the pyridine bands upon complexation with a variety of metal ions.[14] From their data one can estimate in which direction and by approximately how much a given band will be shifted in metal complexes. Carrying this over to the corresponding bands in H_2PDC, the correlation with the appropriate peaks in $Na[Cr(PDC)_2]\cdot1.5H_2O$ is generally unambiguous. The remaining peaks are then easily sorted out. In Table III this correlation

---

(8) W. E. Coleman and L. S. Forster, *J. Lumin.*, **4**, 429 (1972).

(9) R. A. Condrate and L. S. Forster, *J. Chem. Phys.*, **48**, 1514 (1968).

(10) H. J. Schenk and W. H. E. Schwarz, *Theor. Chim. Acta.*, **24**, 225 (1972).

(11) W. N. Shepard and L. S. Forster, *Theor. Chim. Acta*, **20**, 135 (1971).

(12) C. D. Flint and P. Greenough, *J. Chem. Soc., Faraday Trans. 2*, 897 (1972).

(13) R. A. Condrate and K. Nakamoto, *J. Chem. Phys.*, **42**, 2590 (1965).

(14) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

Table V. Analysis of Fine Structure in Phosphorescence Spectra of $Na[Cr(PDC)_2]\cdot 1.5H_2O$ and $K[Cr(MIDA)_2]$

	$\bar{\nu}_0 - \bar{\nu}$		Assignment	
Peak no.	$Na[Cr(PDC)_2]\cdot 1.5H_2O$	$K[Cr(MIDA)_2]$[a]	$Na[Cr(PDC)_2]\cdot 1.5H_2O$	$K[Cr(MIDA)_2]$
		−427		213 (ir) × 2
		−216		213 (ir)
1	−162		162 (ir)?	
2	0		O–O line	
3	39		40 (R)	
4	87		90 (R)	
5	213		213 (ir)	
6	244		213 (ir) + 32 (R)	
7	323	(320)	213 (ir) + 113 (R)	213 (ir) + 107 (R)
8	360	(361)	213 (ir) + 113 (R) + 32 (R); 361 (ir)	213 (ir) + 107 (R) + 38 (R)
9	424	(434)	213 (ir) × 2	430 (ir), 213 (ir) × 2
10	466		213 (ir) × 2 + 32 (R)	
11	553	(535)	443 (ir) + 113 (R)	430 (ir) + 107 (R)
12	636	631	213 (ir) × 3	213 (ir) × 3
13	678		676 (ir)	
		734		740 (ir)
14	763		676 (ir) + 90 (R)	
		798		740 (ir) + 60 (R)
15	847	842	847 (ir)	740 (ir) + 107 (R)
16	897	883	443 (ir) + 453 (R)	740 (ir) + 107 (R) + 38 (R)
		921		916 (ir)
		954		960 (ir)
17	982		527 (ir) + 453 (R)	
		1007		1008 (ir)
		1055		960 (ir) + 92 (R)
		1063		213 (ir) × 5
18	1096	1097	1087 (ir)	1091 (ir)

[a] Values in parentheses are taken from the reflectance spectrum.

is exhibited together with the data for one pyridine complex, $Ni(py)_4Br_2$, from the work of Gill, *et al.*,[14] as an example for coordinated pyridine.

A similar correlation can be made between the ir bands of H_2MIDA and $K[Cr(MIDA)_2]$ with somewhat less confidence. In general, there seemed to be a 1:1 correspondence with occasional extra splitting in the complex or in the free acid. This correlation is also given in Table III.

Now upon examination of Table III, one procedure for the identification of possible candidates for coupling in the luminescence spectrum is to select those bands in the ir spectrum of the complex which are new (in comparison with H_2PDC) or which at least are strongly shifted. It is useful to divide the latter into two categories, bands derived from pyridine, which should represent Cr–N modes, and those unrelated to pyridine bands, which should represent mainly Cr–O modes. Then we have new bands, 361, 744 cm^{-1}; Cr–O type, 527 cm^{-1}; and Cr–N type, 443, 676, 774 cm^{-1}.

The 443-, 527-, and 676-cm^{-1} frequencies appear to be represented in the luminescence. It is also possible that the 744- and 774-cm^{-1} modes participate in the phosphorescence, since the peak observed at 763 cm^{-1} was rather broad and may have included several vibronic transitions. The 361-cm^{-1} frequency represents most likely a metal-nitrogen stretching mode and is probably weakly represented in the luminescence spectrum, where it coincides, however, with a combination band derived from the 213-cm^{-1} mode.

It is tempting to assign the 744-cm^{-1} frequency to a mode involving the Cr–O bond, since a corresponding frequency, 740 cm^{-1}, is prominent in the $K[Cr(MIDA)_2]$ luminescence spectrum and strongly shifted, if not new, in the ir spectrum. To support this we note that Condrate and Nakamoto have observed a band, attributed to a C=O in-plane bending mode, near 740 cm^{-1} in a variety of glycine complexes.[13] There was also found to be strong metal-oxygen participation in this mode.

4. **Pseudo-Stokes Shift.** In $K[Cr(MIDA)_2]$ the maximum of the emission band envelope occurs at roughly 1150 cm^{-1} from the O–O line. We have referred to this displacement as the pseudo-Stokes shift.[1] It is interesting to note that we encounter no measurable pseudo-Stokes shift for $Na[Cr(PDC)_2]\cdot 1.5H_2O$. Practically the only tangible difference between these two compounds is that MIDA adopts a facial configuration, permitting a center of symmetry, while PDC adopts a meridional configuration. It is, however, difficult to explain an effect of this magnitude on the basis of these considerations.

It seems more likely to us that emission results from different excited states in the two compounds. Octahedral Cr(III) phosphorescence spectra are always discussed in terms of the ^2E_g excited state which has been calculated to lie lower than the nearby $^2T_{1g}$ state by some 500 cm^{-1}.[15] However, under conditions of lower symmetry both of these states are split, the $^2T_{1g}$ level to a greater extent, with the result that, for large Dt, the $^2E_g(D_{4h})$ substate of the $^2T_{1g}(O_h)$ level lies lowest.[6]

One case where emission has already been assumed to occur from the $^2T_{1g}$ level is *cis*-$Li[Cr(IDA)_2]\cdot 2.5H_2O$.[1] Here "normal" phosphorescence occurred at temperatures around 200°K, while a different, considerably shifted phosphorescence pattern was observed at 85°K. This led us to conclude that the lowest $^2T_{1g}$ substate lies very close in energy to the lowest ^2E_g substate in *cis*-$Li[Cr(IDA)_2]$, so that electrons can become trapped in the $^2T_{1g}$ potential well at lower temperatures. It was also concluded that the $^2T_{1g}$ substate was moderately shifted radially so that a pseudo-Stokes shift results.

Thus, it may be true that in $K[Cr(MIDA)_2]$, for which Dt should be about twice as large as for *cis*-$[Cr(IDA)_2]^-$, the lowest doublet state is derived from the $^2T_{1g}$ state, while in

---

(15) A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

Na[Cr(PDC)$_2$]·1.5H$_2$O it is derived from the ^2E_g state. Certainly *Dt* is larger in the MIDA than in the PDC complex, since *Dq* for pyridine is much closer to that for carboxylate than is *Dq* for an imino nitrogen, and *Dt* is proportional to the difference between *Dq*(N) and *Dq*(O).

5. **Summary.** In interpreting the luminescence spectrum of Na[Cr(PDC)$_2$]·1.5H$_2$O we have also attempted to cast some light on the character of the vibrational modes involved. The validity of this approach depends on the assumption that vibrational modes involving the metal atom are most strongly coupled to the electronic transition. We have offered some evidence from infrared spectra that this is the case for the PDC complex. A structure determination and normal coordinate analysis would be required, however, to develop a more precise relationship.

Registry No. Na[Cr(PDC)$_2$], 40354-84-5; K[Cr(MIDA)$_2$], 29362-25-2.

Acknowledgments. We thank Mr. Jurgen Zehnder for measuring the Raman spectra and the Deutsche Forschungsgemeinschaft, Bad Godesberg, W. Germany, for financial support.

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90007

Mechanism of Photosubstitution in Chromium(III)-Acidoamine Complexes

CHARLES KUTAL and ARTHUR W. ADAMSON*

Received March 27, 1973

A detailed photochemical study of *cis*- and *trans*-[Cr(cyclam)Cl$_2$]$^+$ and *trans*-[Cr(2,3,2-tet)Cl$_2$]$^+$ (where cyclam is 1,4,8,11-tetraazacyclotetradecane and 2,3,2-tet is 1,4,8,11-tetraazaundecane) is reported. Phosphorescent emission maxima and lifetime data for the complexes are also included. The present results, in conjunction with those from earlier studies, are used to evaluate several alternative excited-state reaction mechanisms for chromium(III) acidoamines. The mechanism most consistent with the data involves a trans attack by an incoming solvent molecule; some degree of bond making in the rate-determining step is also indicated. For *trans*-[CrN$_4$Cl$_2$]$^+$ complexes (where N$_4$ = 4NH$_3$, 2en, 2,3,2-tet, or cyclam), a correlation between the quantum yields and thermal rate constants for chloride aquation is noted.

Introduction

The photochemistry of chromium(III)-acidoamine complexes on irradiation of the d-d or ligand field bands ($^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ in O_h symmetry, here designated $^4L_1$ and $^4L_2$, respectively) has generally been one of substitution by solvent.[1,2] Frequently, the predominant photochemical reaction does not occur thermally, indicating that the excited state involved possesses a chemistry distinct from that of the ground state. While considerable debate has centered on the identity of this reactive state, recent sensitization and luminescence quenching studies strongly suggest that the thermally equilibrated first quartet excited state, $^4L_1{}^0$, is the immediate precursor to photoreaction.[3,4]

The characteristics of quartet excited states which enhance their reactivity relative to the ground state have been discussed in detail elsewhere.[5-7] Briefly, irradiation in $^4L_1$ or $^4L_2$ promotes an electron from a nonbonding or weakly π-(anti)bonding t_{2g} orbital to a strongly σ-antibonding $e_g{}^*$ orbital.[8] This redistribution of electron density weakens the metal-ligand bonds (in some cases leading to considerable distortion from ground-state geometry)[9,10] and renders the complex susceptible to chemical reaction.

On a more detailed level, however, very little is known about the *mechanism* of the excited-state reaction; that is, the sequence of steps leading from $^4L_1{}^0$ to the final photoproduct. The importance of mechanistic considerations can be inferred from our recent study of *trans*-[Cr(cyclam)Cl$_2$]$^+$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[11] Irradiation in the quartet region results in a quantum yield for chloride release ~10^3 times smaller than found for the electronically and geometrically similar *trans*-[Cr(en)$_2$Cl$_2$]$^+$.[12] Further, the geometry of aquochloro product is predominantly trans for the former and cis for the latter compound. The imposition of the stereoretentive cyclam ring markedly affects the reactivity of the excited state, a result which would have been impossible to predict solely on the basis of ligand field strength considerations.

To gain further insight as to the nature of the excited-state reaction mechanism of chromium(III) acidoamines, we report here a detailed photochemical and photophysical study of *trans*- and *cis*-[Cr(cyclam)Cl$_2$]$^+$ and *trans*-[Cr(2,3,2-tet)Cl$_2$]$^+$ (2,3,2-tet = 1,4,8,11-tetraazaundecane). The 2,3,2-tet complex lies between those of cyclam and en in the degree of chelation or ring stricture about the metal atom and thus

---

(1) A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, 68, 541 (1968).

(2) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds," Academic Press, New York, N. Y., 1970.

(3) J. Martin and A. W. Adamson, *Theor. Chim. Acta*, 20, 119 (1971).

(4) S. Chen and G. B. Porter, *Chem. Phys. Lett.*, 6, 41 (1970).

(5) A. W. Adamson, *J. Phys. Chem.*, 71, 798 (1967).

(6) G. B. Porter, S. Chen, H. L. Schlafer, and H. Gausmann, *Theor. Chim. Acta*, 20, 81 (1971).

(7) J. I. Zink, *J. Amer. Chem. Soc.*, 94, 8039 (1972).

(8) This description applies rigorously only to O_h complexes. For lower symmetries, specific axes in the molecule are preferentially labilized, depending upon the orbital splitting pattern (*cf.* ref 7).

(9) G. B. Porter and H. L. Schlafer, *Z. Phys. Chem.* (*Frankfurt am Main*), 37, 109 (1963).

(10) S. Chen and G. B. Porter, *J. Amer. Chem. Soc.*, 92, 2189 (1970).

(11) C. Kutal and A. W. Adamson, *J. Amer. Chem. Soc.*, 93, 5581 (1971).

(12) A. D. Kirk, K. C. Moss, and J. G. Valentin, *Can. J. Chem.*, 49, 1524 (1971).