Luminescence Spectra of Trans-Bis(N-Alkyliminodiacetato)-Chromate(III) Complexes

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Luminescence spectra at 85 K have been recorded for a series of chromium (III) complexes with alkyliminodiacetates (RIDA) of the form K[Cr(RIDA)$_2$], R = M (methyl), E (ethyl), n-P (n-propyl), i-P (isopropyl), n-B- (n-butyl), and t-B (t-butyl). Infrared and far infrared spectra of room temperature samples were also recorded.

All of the RIDA complexes exhibited the vibronic spectrum, with a remarkable shift of the intensity maximum away from the zero phonon line, which is characteristic of trans geometry in these complexes pointing to a ^2E (tetragonal symmetry label) luminescent state. A comparison of vibronic intervals with IR data suggests several bands which may be indicative of iminodiacetate coordination.

I. Introduction

Chromium complexes with iminodiacetate, IDA = [HN(CH$_2$COO)$_2$]$^{2-}$, and related complexes have recently attracted interest directed towards their luminescence spectra [1 – 4]. In addition to the general interest in proto-amino acid complexes, which can serve as models for more complex interactions of metals with peptides and proteins, the luminescence spectra of IDA-type complexes have evinced a number of unusual or unexpected properties.

The breakdown of Schläfer's Rule [5], predicting from the visible absorption spectrum whether phosphorescence or fluorescence should be observed for a given Cr(III) complex, was first pointed out in connection with IDA-type complexes [1], a result which has proved to be general for low symmetry Cr(III) complexes. The MIDA complex (H$_2$MIDA = methyliminodiacetic acid), in which the nitrogens are trans, exhibited a sharp line phosphorescence spectrum, with maximum band intensities occurring some distance from the zero phonon band [1], which was explained in terms of a crossover of the excited doublet states in complexes of appropriately low symmetry [6], whereby the tetragonal ^{2}E state, with an electron configuration different from the ground state, becomes the lowest lying excited state [2]. Such behavior was later noted for other Cr(III) complexes [7]. In addition the [Cr(IDA)$_2$]$^-$ complex, with cis configuration, has itself displayed a number of unusual features: at 85 K on solid samples a fluorescence spectrum was observed, overlaid in some cases with a sharp line phosphorescence. In a glass solution, or with solids at higher temperatures, the overlaid phosphorescence disappeared, while another phosphorescence peak appeared, blue-shifted from the fluorescence [1]. This led to some confusion as to the location of the electron origins in these spectra.

In our original work [1 – 3], we assigned the electronic origins at 14 340 cm^{-1} for cis-Na[Cr(IDA)$_2$] and 14 250 cm^{-1} for trans-Na[Cr(MIDA)$_2$]. The electronic states (using tetragonal symmetry designations) were thought to be ^{2}A$_1$ or ^{2}B$_1$ and ^{2}E, respectively. In both cases weak luminescence bands were located at these positions, although stronger bands were apparent elsewhere. In absorption (diffuse reflectance spectroscopy was used) a corresponding peak was found for the IDA complex, but not for the MIDA complex, where our spectrum extended from 14 550 to 15 900 cm^{-1}. In the latter case this was explained in terms of a pseudo-Stokes shift attributable to the ^{2}E luminescent state, shifting the maximum intensity of the luminescence spectral envelope to about 13 000 cm^{-1}, 1200 cm^{-1} distant from the 0-0 line, with a similar effect in absorption.

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Flint and Matthews later measured the luminescence and absorption spectra of these complexes at 12 – 21 K, where a number of additional features were evident [4]. The luminescence origin for $[Cr(MIDA)_2]^-$, which was also assigned as ^2E, was placed at 13 402 cm^{-1}. The low temperature absorption spectrum revealed a lower intensity series from 13 402 to about 14 100 cm^{-1} in addition to the spectrum observed by us, so that this assignment must be taken as unambiguous. However, a series of weak bands observed by us a luminescence, between 14 215 and 14 860 cm^{-1}, was found absent by Flint and Matthews at 20 and at 80 K. Since these increased, then decreased in intensity with temperature, they were assigned as hot bands by us. It is difficult to reconcile their existence, though, with a 13 402 cm^{-1} origin.

Cooling to 20 K resulted in the virtual disappearance of the $[Cr(IDA)_2]^-$ fluorescence, with consequent greater detail in the (previously overlaid) phosphorescence spectrum. Again the higher energy emission noted by us around 14 400 cm^{-1} was not observed by Flint and Matthews at temperatures up to 300 K. And again a lower intensity series of bands between 13 200 and 13 600 cm^{-1} was apparent in absorption spectra at 20 K. Two prominent peaks in luminescence and absorption were assigned as ^2E electronic origins, at 13 190 and 13 355 cm^{-1}, from two non-equivalent crystalline sites [8]. A room temperature X-ray structure has since been performed on $K[Cr(IDA)_2]$. There do appear to be two non-equivalent Cr sites, however the non-equivalence is due entirely to the arrangement of the waters of crystallization, from which it is difficult to explain this large difference in 0-0-frequencies [9, 10].

The greater detail from the low temperature spectra, especially the low energy region of the absorption spectrum, not seen in the 80 K diffuse reflectance measurements, lends a good deal of plausibility to these assignments, especially for $Na[Cr(MIDA)_2]$, although some of the discrepancies remain puzzling.

These discrepancies are most pronounced in the IDA complex, with a cis configuration. Recently we reported the synthesis of several further homologs; involving ethyl, n-propyl, i-propyl, n-butyl, and t-butyl derivatives of iminodiacetic acid [11]. In this paper we report the details of their luminescence, IR, and far-IR spectra.

If one of these complexes were to have adopted a cis configuration some of the more important discrepancies might have been cleared up. But all were found only in the trans geometry. Our results tend to confirm the electronic assignments of Flint [4], but beyond that, by observing the variations in vibronic frequencies over a homologous series, a kind of "fingerprint" for iminodiacetate coordination can be discerned.

II. Experimental

$K[Cr(EIDA)_2]$, $K[Cr(n\text{-}PIDA)_2]$, $K[Cr(i\text{-}PIDA)_2] \cdot 2.5\,H_2O$, $K[Cr(n\text{-}BIDA)_2]$, and $K[Cr(t\text{-}BIDA)_2] \cdot 2.5\,H_2O$ (E = ethyl, P = propyl, B = butyl) were prepared as previously described [11].

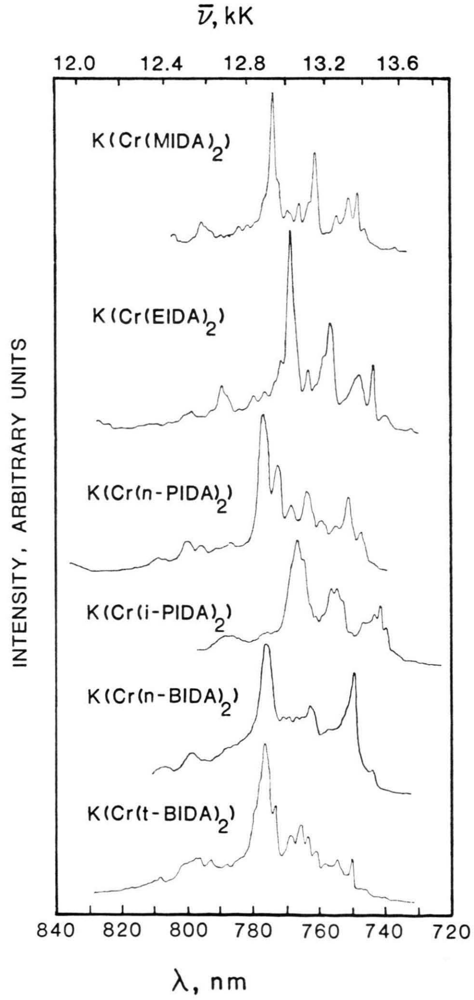

Fig. 1. Luminescence spectra at 80 K of alkyliminodiacetate complexes of Cr(III).

Table 1. Luminescence data ($^2E \rightarrow {}^4B_1$) for $K[Cr(RIDA)_2]$ complexes at 85 K. Vibronic intervals, $\bar{\nu}_0 - \bar{\nu}$, in cm^{-1}. Anti-Stokes bands expressed as $\bar{\nu} - \bar{\nu}_0$, where $\bar{\nu}_0$ is the frequency of the zero phonon transition.

	M	*E*	*n – P*	*i – P*	*n – B*	*i – B*
0–0	13435	13514	13328	13495	13346	13336
			16 w	32 m	28 w	29 w
	45 s					56 w
	81 w	77 s	67 w	70 w	70 vw	79 w
	113 m	102 m		92 w	112 vw	107 vw
			127 w			124 vw
			146 w		139 vw	143 vw
	163 w			160 w	159 vw	
			186 w			
	213 m	223 s	211 s	206 m	212 w	206 w
	225 vs	237 s	227 s	238 s	238 s	249 m
	258 m	269 m	253 w	260, 266 s	281 w	281 s
	306 m	311 w	302 m	316 w	306 m	299 m
						324, 334
	353 m	349 m	353 m	346 w	346 m	347 w
	366 m		373 s	370 w	376 m	
	418 s	420 m	420 m	409 s	409 w	398 s
				430 w	431 m	435 s
	443 vs	440 vs	443 vs	440 vs	451 vs	452 vs
			456 m			
	487 m	491 m		476 w	469 m	482 s
					525 vw	506 m
		540 w				
	570 w	586 w		592 w	573 vw	
	611 w					
		644 w	631 w		626 w	637 w
	667 w				655, 677	661 w
	703 w		694 w			692 w
		715 w			713 w	715 w
	751 w				756 w	743 w
	777 w	778 w	765 w	767 m		769 w
	798 m	803 m		797 m	794 vw	789 w
					821 m	823 w
	843 w	853 w	834 m	843 w	846 w	841, 859
	894 w	881 w				898 w
		910 w	909 w			917 w
	927 w	931 w	929 w		928 w	
	943 w	955 w	946 w		954 w	955 w
	965 w	967 w	972 w	968 w	974 w	985 w
				1001 w		1005 vw
	1014 w					1019 vw
		1040 w	1037 w		1045 vw	1061 vw
	1101 w	1090 vw		1063 w	1071 vw	1087 w
		1115 w	1112 vw	1106 w		
	1153 w	1135 w		1143 w	1131 vw	
	1188 vw	1177 w		1169 w		
				1207 w	1195 vw	
	1256 vw	1247 vw		1245 w		1235 vw
		1280 vw		1274 w		
	1312 w	1316 w	1303 w	1312 w	1324 w	1321 w
	1348 w		1330, 1348	1344 w		
		1362 w		1360 m		1368 w
				1378 w	1383 w	
				1405 w		1410 vw
			1484 w			
		1572 vw	1567 vw	1593 w		1577 vw
		1628 w	1609 vw	1618 w		1630 vw
	1642 w	1640 vw	1650 w	1656 w		1651 w
		1663 vw				
	1703 vw	1709 vw	1715 vw			1709 vw
		1797 vw		1806 w		
	1821 vw	1825 vw				
		1917 vw				
	1977 vw	1988 vw				
		2002 vw				
		2029 vw				
Anti-Stokes Bands						
	40		25	23		38
	83	64	66		69	76
	112	101	86		100	110
			122			123
	157	158	151	163		140
			182	191		185
			198		200	
	209	211	226	222		227
	254		265	262		255
			280		283	
		313				310
		348				333
			401			397
	415	416	420			417, 425
			426			
			509			

Infrared spectra were recorded on KBr pellets with a Perkin-Elmer 457 IR spectrometer. Far infrared spectra were measured on a Beckman FIR-720 interferometer, using polyethylene pellets. The instrumentation for luminescence spectroscopy employed argon ion laser excitation (488 and 363.8 nm) and a Spex 1700-II 0.75 m monochromator, and has been described in detail elsewhere [1, 12]. Luminescence spectra were recorded on solid, polycrystalline samples at 85 K.

III. Results

The luminescence spectra at 85 K of all the N-alkyliminodiacetato complexes studied resembled the spectrum of $[Cr(MIDA)_2]^-$, and are displayed in Figure 1. The electronic origins are readily identified as the first (highest energy) intense band in each spectrum. As was the case with $[Cr(IDA)_2]^-$ and $[Cr(MIDA)_2]^-$, no discernible features in the 85 K diffuse reflectance spectra were observed in the region of the luminescence electronic origins [1], although several bands at higher energy were evident. Thus direct evidence for the correctness of

Table 2. Higher energy luminescence spectrum, possibly $^2A_1$ or $^2B_1$, frequencies in cm^{-1}.

Mg[Cr(IDA)$_2$]^a	14378	14472		
Na[Cr(IDA)$_2$]^a	14463	14656	14860	
K[Cr(MIDA)$_2$]^a	14493	14704		
K[Cr(MIDA)$_2$]^b	14186	14259	14413	14451
Na[Cr(MIDA)$_2$]^a	14215	14463	14656	14860

[a] Reference [1]. [b] This work.

the zero phonon band assignments is lacking, and indirect evidence from the internal vibronic structure must be relied upon for confirmation.

Only in one of the complexes, K[Cr(MIDA)$_2$], was a reproducible series of weak bands at higher energy recorded, similar, but not identical, to bands previously observed in this region [1]. The luminescence data are tabulated in Table 1 in the form of vibronic intervals from the electronic origin, which is assigned [2, 4] to the $^2E \rightarrow {}^4B_1$ transition. The higher energy spectrum for K[Cr(MIDA)$_2$] is tabulated in Table 2 and compared with previous data for IDA and MIDA complexes. Infrared and far infrared data up to 2000 cm^{-1} are presented in Table 3. A typical far infrared spectrum, that for K[Cr(t-BIDA)$_2$], is displayed in Figure 2.

IV. Discussion

Even without the low energy part of the absorption spectrum (the part which overlaps with luminescence) to establish correspondences and determine the location of the 0-0-lines, the internal correlations among vibronic intervals leave little doubt that they have been properly assigned. Their positions are consistent with the assignment of Flint and Matthews [4] for Na[Cr(MIDA)$_2$].

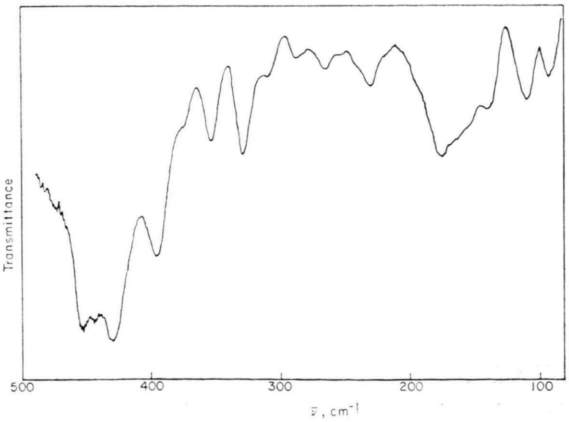

Fig. 2. Far infrared spectrum (room temperature) of K[Cr(t-BIDA)$_2$] dispersed in polyethylene.

Table 3. Infrared spectra of iminodiacetato complexes of the type K[Cr(RIDA)$_2$], $T = 295$ K, data in cm^{-1}.

R = H	*M*	*E*	*n* – *P*	*i* – *P*	*n* – *B*	*t* – *B*
86 m	87 w	87 m		88 m	94 w	93 w
	106 s	110 w		112 w		110 w
	122 a	126 w	122 s		120 s	
142 w			142 w	137 m	136 w	138 w
160 w	152 m	165 m	164 w	171 w		175 m
				190 m		
	217 s	222 m	208 m		206 m	
235 m			232 m	234 m		230 m
265 m	254 s	264 m		268 w	250 m	265 w
			288 w	288 w		287 w
296 m	310 m	313 w	310 w	317 w	304 w	310 w
				342 m		329 s
370 m	365 m	351 s	365 w	375 w	365 m	352 m
		399 m	413 w	404 w	414 w	396 m
414 w	418 w	421 m	435 s	426 m		444 s
						444 m
430 s	440 s	437 s	448 s	442 s	443 s	445 s ?
495 w	480 m	485 s		467 w		
526 s	528 m	521 m	517 s	503 m	515 m	510 w
		555 w				
584 m	570 w	568 w	571 s	563 w	569 m	567 m
				588 m		585 w
		628 w	618 m	633 w	612 m	632 m
						709 m
745 vs	746 s	735 m	741 s	733 m	742 m	
		748 w	751 w	755 m	758 m	762 m
						782 s
		826 w		837 s		857 s
		882 m	880 m			
893 vs	900 m		895 w	906 w		
917 vs	921 m	911 s	915 s	916 s	920 s	912 s
		930 s	928 s		934 m	942 m
945 w	938 w	952 w	943 m	940 m	959 m	952 m
958 m	964 w	973 w	973 s			982 m
	986 w			988 m		
1018 s	1011 m	1024 m	1032 s		1012 m	1018 w
				1038 w	1040 m	1035 m
				1058 w		1056 w
1086 s	1095 m	1085 m	1088 m	1083 m		
	1150 m	1122 m	1110 w	1138 s	1114 m	
		1170 m		1184 w		1180 s
1230 w		1240 m	1228 s	1240 s	1220 m	1228 s
	1250 w				1255 m	1245 s
1268 w		1280 w	1282 m	1275 w		1263 w
1319 vs	1303 m	1310 m	1307 vw	1309 w	1322 w	1311 m
		1340 m	1326 m	1330 m	1333 w	1326 m
			1350 s	1350 ws		1355 w
1355 vs	1262 vs	1375 s	1368 s	1370 w	1365 vs	1374 vs
			1390 s	1385 s	1385 m	1403 w
			1429 m	1435 w	1428 m	1436 w
		1442 w	1445 w			
			1460 m			
1480 w	1460 m	1473 w	1470 s	1470 w	1470 m	1475 m
1645 vs	1631 vs	1631 vs	1640 vs	1624 vs	1645 vs	1635 vs
		1658 w		1658 m		1650 s

The weak bands observed in luminescence some 700 – 1200 cm^{-1} higher than the $^2E \rightarrow {}^4B_1$ origin are problematic. These were observed only for the MIDA complex. They do not correspond to bands observed in reflectance spectra, which were found at still higher energy. The possibility that they represent anti-Stokes emission from excited ^2E vibrational levels seems remote, since the intensities are several orders of magnitude greater than the Boltzmann factors would indicate. There is the possibility that they represent emission from another doublet ($^2A_1$, $^2B_1$?), not necessarily including the zero phonon line. From Flint's data [4], the transition probabilities in absorption are evidently much greater between ground state and the upper doublets than between the ground state and the luminescent state, ^2E, since the higher energy bands are much more intense. This may very well be the case in emission as well, yielding abnormally high intensities from the higher energy doublets (though still low relative to $^2E \rightarrow {}^4B_1$). It is, however, troubling that there is no coincidence with absorption bands to support this kind of argument.

In the case of the IDA complex, however, the coincidence between luminescence and absorption is present, and there can be little doubt that emission from a higher excited doublet is involved. No conclusive evidence as to the identity of these excited doublets has been offered as yet. It remains an interesting problem to account for the dependence of the relative emission intensities from the two doublets on the temperature and the environment of the complex ion. For example, in frozen solution at 85 K the higher energy phosphorescence is most intense, which is an unusual occurrence among Cr(III) complexes.

The vibronic data in Table 1 and the infrared data in Table 3 are arranged so as to suggest correspondences among the complexes studied. The clear correspondences in the luminescence spectra confirm the assignments of the electronic origins.

Beyond this it is our goal to establish a basis by which the coordination environment around the metal center may be identified using the vibronic data from the luminescence spectrum. In the present context it would be useful to find several prominent bands of relatively constant frequency, which would be characteristic of iminodiacetate coordination in general. And also bands which vary systematically with the N-alkyl group are desirable in order to further characterize the coordination environment. A separation of the imino nitrogen contributions from those of the carboxylates would be helpful, but strong mixing of the low frequency vibrational modes makes this a largely unrealistic goal. On the other hand, certain ring deformation modes may indeed offer some clues as to the nature of the chelating ligand.

Several interesting features are apparent upon detailed comparison of vibrational frequencies in infrared and in luminescence. To some extent these comparisons are flawed because the spectra were recorded at different temperatures and in different environments (pure solid vs KBr pellet). Nor are the suggested correlations through the homolog series in every case defensible.

Nevertheless, one notes that certain modes are more prominent, and more likely to be found for each complex in the series, in the luminescence spectrum, while others are better located in the IR spectrum.

A facile explanation would be that vibrations involving the metal atom should be most prominent in luminescence [13, 14], and indeed it appears that metal atom participation plays a considerable role. Between 200 and 500 cm^{-1}, where the stretching and bending modes of the octahedral skeleton are to be found, the luminescence spectra appear much more complete than do the IR spectra, with several features prominent in luminescence, and weaker or absent in IR.

Below 200 cm^{-1}, however, where lattice modes, as well as some of the ring deformations, should be located, the IR spectrum appears more complete, and the correlation between IR and luminescence is not at all apparent. For example, a strong IR band near 122 cm^{-1} is found in all complexes with n-chain alkyl groups. No corresponding feature is to be found in the luminescence spectrum.

One problem which must be faced in interpreting a vibronic spectrum is that of deciding which bands represent fundamentals and which are combination frequencies, since combination bands are allowed in vibronic spectra. In general fundamentals are more intense, although relative intensity is an unsure guide in spectra which cover a range of four or five orders of magnitude in intensity. And, of course, the question of metal atom participation comes up again, suggesting that the intensity of a ligand fundamental vibration be proportional to the extent to which that vibration is mixed with another vibration involving the metal atom.

For example, the methyl and methylene H – C – H bending vibrations, at around 1380 and 1470 cm^{-1}, respectively, are prominent in the IR spectrum, and consistent throughout the series. In the luminescence spectrum there is little trace of these modes, presumably for lack of effective coupling to the metal center. On the other hand, the asymmetric carboxylate stretching frequency, in the infrared found near 1630 cm^{-1}, is also prominent in the luminescence spectra. Here the proximity to the metal atom establishes a basis for coupling with the metal-oxygen stretch.

In the region between 500 and 1650 cm^{-1}, most of the well-defined (i. e., present for most of the members of the series) luminescence bands can be attributed to fundamentals. For example, the band near 1310 cm^{-1} in luminescence correlates well with the IR frequencies (see Table 4). This mode does not appear to involve the carboxylate portion of the ligand [15], and may therefore be a C-N stretch. This particular mode may serve to indicate the presence of an imino nitrogen.

In the metal-ligand portion of the spectrum we find several prominent features. Two bands near 220 cm^{-1} appear very characteristic of iminodiacetate coordination. These frequencies can most probably be assigned to ring deformation modes. Similarly intense bands can be found in the luminescence spectra of oxalato complexes [14], around 230 cm^{-1}, and amino acid complexes [16], around 190 cm^{-1}. Comparison of IR and luminescence (see Table 4) indicates that this pair of bands is much more readily identified in luminescence.

Another strong band, consistently seen in luminescence, lies around 440 cm^{-1}, and may be associated, at least partly, with the metal-oxygen stretch [17, 18]. Although very prominent in luminescence, this vibration likewise gives rise to an intense band in IR (Table 4).

Table 4. Comparison of vibrational frequencies in luminescence and IR for certain modes in K[Cr(RIDA)$_2$]. IR spectra of KBr pellets at 295 K, luminescence of powdered solid at 85 K.

	R=	M	*E*	*n – P*	*i – P*	*n – B*	*t – B*
ν_1	Lum	1312	1316	1303	1312	1324	1321
	IR	1303	1310	1307	1309	1322	1311
ν_2	Lum	213	223	211	206	212	206
	IR	217	222	208	—	206	—
ν_3	Lum	225	237	227	238	238	249
	IR	—	—	232	234	—	230
ν_4	Lum	443	440	443	440	451	452
	IR	440	437	448	442	443	454

Previous work suggests we might find the metal-nitrogen stretch between 500 and 600 cm^{-1}[14] as in ethylenediamine complexes [19], although there is no direct basis for extrapolating to $\nu(\mathrm{Cr-N})$ for an imino nitrogen. There are two well-defined IR bands in this region, one near 570 cm^{-1}, which is nearly constant across the series. and another near 520 cm^{-1} which is subject to considerable variation. This latter behavior is what is expected for the metal-nitrogen stretch, but it is worrisome that neither of these two bands appear more than sporadically in the luminescence spectra. It has been observed [14] that metal-ligand stretching modes no not contribute as much to the intensity in luminescence as do bending modes, but one would expect that $\nu(M-N)$ would at least be consistently present.

Several other well-defined bands in luminescence might involve the metal-nitrogen stretch. Most of the bands in the 300 – 500 cm^{-1} region do not seem to exhibit large variations in frequency through the series, although several seem to undergo some splittings, making correlations between luminescence and IR difficult. This behavior may indeed be indicative of $\nu(M-N)$, and in this regard the band at 400 – 420 cm^{-1} in luminescence might be tentatively suggested to be the stretching frequency. A definitive answer to this question will have to await isotope studies, as will the related problem of combination band assignments.

Several well-defined bands in the luminescence spectra have no counterparts in IR and must be combination bands. The selection rules for vibronic and IR spectra are different, but there is little reason to expect large differences for low symmetry molecules such as these. The bands near 1580 and 1710 cm^{-1} are rather clear examples of combinations, as is probably the band near 795 cm^{-1}. It is not at all clear which combinations are involved, although such information could be extremely useful in structure identification. Again, isotope studies are needed to shed some light on this problem.

V. Conclusion

An examination of a number of homologous alkyliminodiacetato complexes of chromium(III) confirms, in general, the assignment of Flint for trans complexes with IDA type ligands [4]. Still, looking at the entire range of luminescence data on IDA complexes reported thus far, some questions are still open.

1. Is the high energy luminescence spectrum ($14\,200-14\,860\ \mathrm{cm}^{-1}$) repeatedly observed for MIDA and IDA complexes at 85 K real, perhaps representing emission from an excited doublet?

2. It seems quite peculiar to find the electronic origins assigned to $^2E \rightarrow {}^4B_1$ transitions for both cis and trans complexes, and at approximately the same energy, $13\,402\ \mathrm{cm}^{-1}$ for trans-Na[Cr(MIDA)$_2$], 13 355 and $13\,190\ \mathrm{cm}^{-1}$ for cis-Na[Cr(IDA)$_2$], in particular, in view of the fact that the two bands of the latter compound should originate from the existence of two non-equivalent sites in the lattice. The $^2A_1$ and $^2B_1$ state (from octahedral ^2E_g) is normally the lowest doublet, and it is only the strong tetragonal field from imino nitrogens and carboxylates which cause the octahedral $^2T_{1g}$ state to split sufficiently that ^2E (from $^2T_{1g}$) can sink to become the lowest energy doublet. But the tetragonal field in the cis should be only about half that in the trans complex, so that, at very least, the ^2E might be expected to occur at a significantly higher energy in the cis complex. Or, perhaps more probably, a double crossover might not properly be invoked at all.

Acknowledgements

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