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Absorption Spectra of Neutral Dipyridyl Complexes*

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Absorption spectra of very air-sensitive Li Dipy, Li$_2$Dipy, Ti Dipy$_3$, V Dipy$_3$, and Cr Dipy$_3$ are reported. The spectra of the first two complexes are characterized by bands with complex structure; the remaining three show electronic transitions at very low energy. In a search for complexes of zero-valent rare-earths, several very air-sensitive dipyridyl complexes of rare-earths were prepared. Of these, spectra are reported for the ytterbium and thulium complexes.

Introduction

In recent years Herzog and coworkers[1] have investigated the reaction products of alkali metals with 2,2′-dipyridyl*** (Dipy) in liquid ammonia and tetrahydrofuran (THF). These products, in particular Li$_2$Dipy, are very powerful reducing agents and as such extremely air-sensitive. Herzog and coworkers have used these reducing agents to obtain a large number of neutral dipyridyl complexes of the type M Dipy$_3$ or M Dipy$_4$, with M a metal, to which Herzog attributed the oxidation state zero.[1-4]

An interesting question concerning these reduction reactions is whether it is actually the central ion M that is reduced, or the dipyridyl ligand. The absorption spectra, together with the magnetic and E.S.R. data already reported,[1] could contribute, in this context, to a better understanding of this class of compounds. Accordingly we report here absorption spectra of Li Dipy, Li$_2$Dipy, V Dipy$_3$, Ti Dipy$_3$, Cr Dipy$_3$, Yb Dipy$_3$, and its Tm analogue.

From a spectroscopic point of view, neutral dipyridyl complexes of rare-earths are quite interesting for the following reason. In the reduction of a trivalent 4f^n ion one would expect either the disappearance, or a drastic change, of its typical line-absorption.

Experimental Section

All the products we shall discuss are very air-sensitive and have to be handled anaerobically. Figure 1 shows a typical reaction arrangement. Figure 2 shows an arrangement for the recovery of solid products from a solution.

The absorption spectra of solutions were taken on a Cary 14 spectrophotometer using flow-cells. Spectra of volatile products were taken with the modified sublimator of Figure 3. Sodium chloride windows made it possible to study the same sample both in the region covered by the Cary 14 and in the infrared region. In the latter case a Perkin-Elmer Spectrophotometer 521 was used. The sublimator of Figure 3 could also be used as a Dewar, for runs at liquid nitrogen temperature.

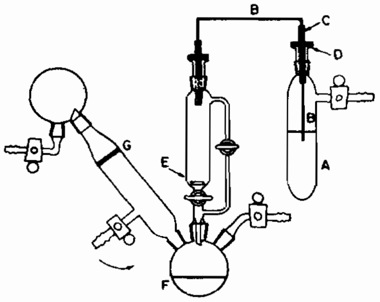

Figure 1. Typical reaction arrangement (schematic). (A) Green THF-solution of Li$_2$Dipy. (B) Polyethylene capillary. (C) Glass capillary; 8 mm O.D. (D) Oil-seal in glass housing. (E) Lithium metal, to convert any Li Dipy to Li$_2$Dipy. (F) THF-suspension of a dipyridyl complex of metal chloride. (G) Sintered-glass filter.

(*) Work performed in part under the auspices of the U. S. Atomic Energy Commission.

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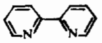
(***) 2,2′-dipyridyl:  usually acts as a bidentate ligand via the two nitrogens.

(1) For a review, S. Herzog and R. Taube, Z. *Chemie*, *2*, 208 (1962).

(2) S. Herzog and W. Schön, Z. *anorg. allg. Chemie*, *297*, 323 (1958).

(3) S. Herzog, G. Byhan, and P. Wulfert, Z. *Chemie*, *1*, 370 (1961).

(4) S. Herzog and K. Gustav, Z. *Naturf.*, *17b*, 62 (1962).

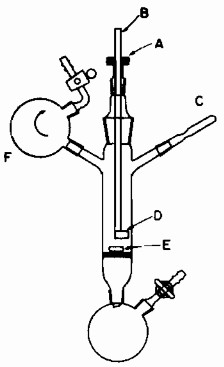


Figure 2. Recovery of crystalline products (schematic). (A) Oil-seal in glass housing. (B) Rod; 8 mm O.D. (C) Glass container for dry product. (D) Scratcher, of magnetic material. (E) Stirring bar. (F) Crystal-containing solution. A vacuum stopcock between C and F is not shown.

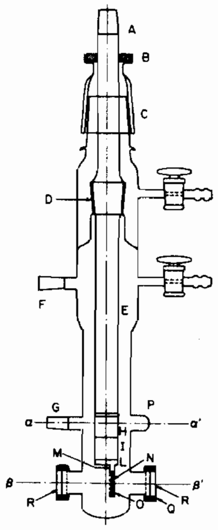


Figure 3. Multipurpose cell for sublimation of very-air-sensitive materials and for their optical and infrared study at room temperature and 78°K. (Schematic). (A) Ground-glass joint Ŧ 19/38 m. (B) Oil-seal in glass housing. (C) Joint Ŧ 45/40. (D) Ŧ 34.5/35. (E) Inner container (Pyrex); 19 mm O.D. (F) Ŧ 14/23 to vacuum gauge. (G) Ŧ 14/23 for introduction of samples. (H) Kovar to Pyrex seal. (I) Copper cup. (L) Copper block. (M) Copper holder for sodium chloride disk. (N) Sodium chloride window. (O) Circular spring. (P) Sample cavity. (Q) Oil-seal in glass housing. (R) Sodium chloride windows. Axis $\alpha - \alpha'$ at 45° with respect to axis $\beta - \beta'$.

Li Dipy and Li$_2$Dipy. These two products have been identified by Herzog.[1] We obtained them by reaction of lithium metal with dipyridyl in liquid ammonia or in freshly distilled ethers, such as tetrahydrofuran and 2-Methyl tetrahydrofuran (MeTHF). Li Dipy is red in THF, MeTHF or liquid ammonia; Li$_2$Dipy is olive green in the same systems.

V Dipy$_3$. Anhydrous V Cl$_3$ was suspended in THF with three equivalents of Dipy and reacted with green Li$_2$Dipy until an intensely blue solution was obtained, in agreement with Herzog's results[5] on the magnesium reduction of [V Dipy$_3$]I$_2$. The reaction was repeated seven times with consistent results. Excess Li$_2$Dipy produced the violet solution identified by Herzog[5] as containing Li[V Dipy$_3$], with a formally V^{1-} ion. Blue V Dipy$_3$ sublimed at $\sim$250°C/10^{-3} torr, in agreement with Herzog's results.[5] The absorption spectra of Figures 8 to 11, in what follows, pertained to samples from different preparations and were consistent. The spectra of the sublimed products were in good agreement with those of THF solutions, indicating that solvation effects were not important.

Ti Dipy$_3$. We repeated three times Herzog's preparation,[6] starting from TiCl$_4$ in THF in the presence of dipyridyl, and found essentially the same reaction behaviour reported by Herzog,[6] including the formation of violet Li[Ti Dipy$_3$]. Blue Ti Dipy$_3$ sublimed at $\sim$250°C/10^{-3} torr. Sublimed films of Ti Dipy$_3$ from three different preparations showed consistent spectra.

Cr Dipy$_3$. Herzog[7] prepared Cr Dipy$_3$ by two routes: (a) by sodium reduction of [Cr Dipy$_3$]Br$_2$ in THF; (b) by disproportionation in water of (Cr ac$_2$.H$_2$O)$_2$ with 1.5 Mol dipyridyl. The sublimed brown product, whose spectrum is shown in Figures 14 to 16, was obtained as follows. Anhydrous CrCl$_3$ was stirred in THF with three equivalents of dipyridyl and reacted with an excess of Li Dipy. The reaction slurry was stirred at room temperature for three days; then the supernatant was removed by anaerobic filtration. The reaction solid was continuously extracted with boiling benzene. The crystals separating out in the extraction vessel were transferred to the sublimator of Figure 3. A brown film of sublimate appeared at approximately the temperature of sublimation of V Dipy$_3$ and Ti Dipy$_3$, at a comparable pressure. This is consistent with Herzog's observations on Cr Dipy$_3$.[2,7]

The spectra of sublimed Cr Dipy$_3$ are contrasted in Figures 14 and 15 with those of a solution obtained as follows. [Cr Dipy$_3$]Br$_2$ in THF was reduced with sodium metal. After 24 h reaction at room temperature, the green slurry was filtered, giving a brown filtrate, changing to red on decomposition. The reaction solid was continuously extracted with boiling benzene. An intensely-coloured brown solution was obtained. This brown solution was used for the spectrum of Figures 14 and 15. There is a fair agreement in the spectra of solution and sublimed film, but some solution peaks in the near infrared could be due to the presence of another phase.

Reactions Involving Rare-earths. Anhydrous rare-earths chlorides were stirred in THF with three equivalents of Dipy and reacted at room temperature with Li Dipy or Li$_2$Dipy. For all of the rare earths in the 4f^n series from Sm to Yb included, the reaction consistently produced an intensely brown solution and a black reaction solid, both of which were very air-sensitive. In the case of Sm and Yb the reaction solid was tested for volatile products, with negative results. In the case of Sm an intermediate reduction

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(5) S. Herzog, *Z. anorg. allg. Chemie, B294,* 155 (1598).

(6) S. Herzog and R. Taube, *Z. anorg. allg. Chemie, 306,* 159 (1960).

(7) S. Herzog, C. K. Renner, and W. Schön, *Z. Naturf., 12b,* 809 (1957).

phase, a green solution in the presence of a green solid, was consistently observed.

With most of the rare-earths ions studied, filtration of the reaction slurry and crystallization of the filtrate at dry-ice temperature gave dark brown crystals. In the case of Tb these crystals were separated and dried in vacuo. The analysis of the black, shiny material obtained gave: 14.10%, Tb; 62.40%, C; 4.85%, H; and 15.18%, N. The analysis suggests the composition Tb Dipy$_4$.

Another reaction route involving Eu and Yb was used. Eu metal or Yb metal, dissolved in liquid ammonia, were reacted with Dipy, giving a reaction product similar in appearance to that found in the reactions involving the chlorides, that is, dark brown solutions and black solids. It was also found that pyrophoric, black Yb metal, as obtained from drying ammoniacal solutions, reacted at room temperature with dipyridyl in THF, in the presence of small quantities of iodine.

Yb Dipy$_3$ was accordingly obtained as follows. Ytterbium metal, dissolved in liquid ammonia, reacted with dipyridyl. The dark-brown reaction slurry was allowed to slowly reach room temperature. It was then refluxed with THF and filtered hot. An aliquot of the dark brown filtrate was treated with de-aired heptane. The resulting precipitate was separated from the supernatant and dried in vacuo at 70°C. The black, shiny product gave on analysis: 27.42%, Yb; 12.03%, N; 3.38%, H. Calculated for Yb Dipy$_3$: 27%, Yb; 13.1%, N; 3.75%, H.

The spectra of Figures 19 and 20 were taken on a portion of the filtrate which had not been treated with heptane. The spectra of Yb are contrasted with those of the brown filtrate from the reaction of anhydrous TmCl$_3$ with Li$_2$Dipy in THF, in the presence of three equivalents of dipyridyl.

The Observed Spectra. Li Dipy and Li$_2$Dipy. Figures 4 and 5 show the absorption spectra of red Li Dipy in MeTHF at room temperature and at 78°K.

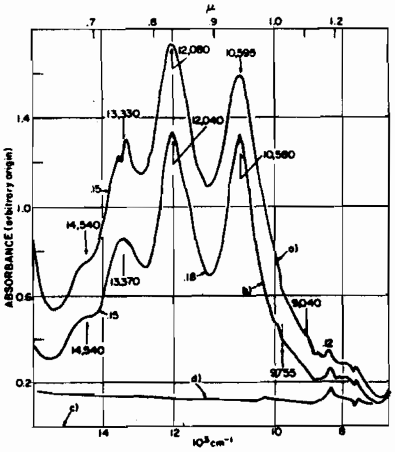

Figure 4. Red Li Dipy in MeTHF. 1 mm flow-cell. (a) At room temperature. (b) At 78°K. (c) Zero line for both curves. (d) Same as (a), but after solution had discoloured on standing. The small differences in the peak positions of (a) and (b) are within the experimental error. The weak peaks at ~8,000 cm⁻¹ are due to the solvent. There is a change in scanning speed at 1 μ. Typical slit-widths in mm units are shown on the curves.

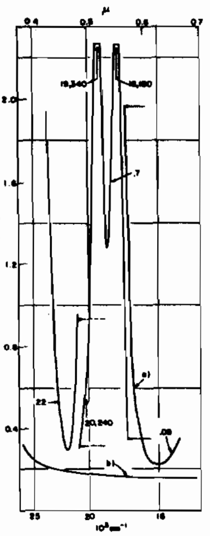

Figure 5. Red Li Dipy in MeTHF; 1 mm flow-cell. Temperature 78°K (Figure 4b continued). Molar absorptivity of peaks estimated as 3×10^3. The baseline is shifted at the position of the horizontal arrows, in order to keep the sharp absorption peaks within the figure. (b) Same as (a), but after the solution had completely discoloured on standing.

The ε values for the two peaks at 18,180 cm^{-1} and 19,340 cm^{-1} are estimated as 3×10^3 liter mol^{-1} cm^{-1} (Figure 5). This is probably a lower limit of the molar absorptivity, because of possible decomposition in the time required to cool the sample down to 78°K. The decomposition product of Li Dipy in THF does not appreciably absorb in the region of interest (Figures 4d and 5b).

At room temperature the near infrared absorption showed a band with four distinct, fairly equidistant peaks. Cooling the solution down to liquid nitrogen did not appreciably change the absorption. This appeared to be generally the case for all of the compounds studied.

The pattern of several absorption peaks separated by 1,300 to 1,400 cm^{-1} (Figure 4) was quite pronounced for green Li$_2$Dipy, where at least seven

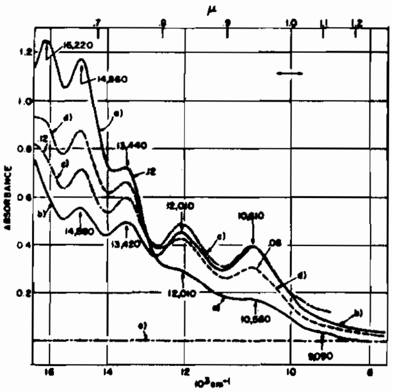

Figure 6. Spectra of Li$_2$Dipy and its decomposition products. 0.1 mm MeTHF solution against 0.1 mm MeTHF. Room temperature. (a) Green Li$_2$Dipy. (b) Same as (a), but 10 minutes later. (c) Solution now red. (d) Still later; orange solution. (e) Extrapolated zero line for all four curves. There is a change in scanning speed at 1 μ. The peak periodicity of ~1,400 cm⁻¹ is quite evident.

such peaks were detected (Figures 6 and 7). Green Li_2Dipy decomposed to red Li Dipy, which in turn decayed to colourless solutions in THF. Changes in the absorption of Li_2Dipy, due to decomposition, are indicated in Figures 6 and 7. For less absorbing samples of Li_2Dipy another band was found at 25,000 cm^{-1}, approximately 50 times more intense than the peak at 17,630 cm^{-1} in Figure 7a.

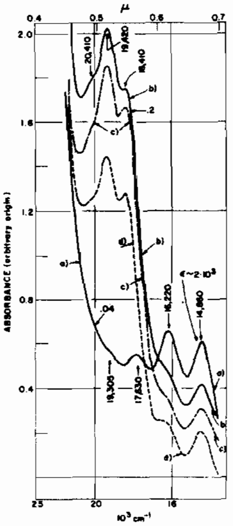

Figure 7. Same as Figure 6, but in the visible region.

V Dipy₃, Ti Dipy₃, and Cr Dipy₃. Sublimed V $Dipy_3$ and Ti $Dipy_3$ were both dark blue and looked very similar on visual inspection. Accordingly their spectra in the visible were not greatly different. In the near infrared region, though, they were distinctly different. In particular V $Dipy_3$ showed an intense absorption band centered at 4,200 cm^{-1}, an unusually low energy for electronic transitions. This band was especially evident in the spectra of sublimed films, where interfering absorptions from the solvent were absent (Figure 8). Indication of this absorption band could also be found in the infrared (sodium chloride region) (Figure 18a). The main outlines of the V $Dipy_3$ spectra were common both to thin and thick films of sublimed material. In more absorbing samples, effects due to the overlap of bands became appreciable (Figure 10). Spectra of a sublimed film of V $Dipy_3$ were also taken at liquid-helium temperature. At low temperature the band at ~4,200 cm^{-1} showed a doublet structure and an additional weaker absorption at higher energies (Figure 9).

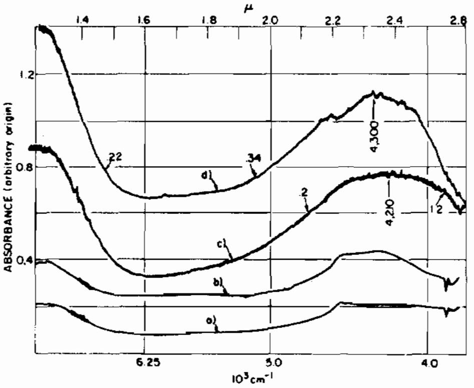

Figure 8. Sublimed films of blue V $Dipy_3$. (a) Room temperature. (b) Same as (a), but at 78°K. (c) Thicker sample from a different preparation. Room temperature. (d) Same as (c), but at 78°K.

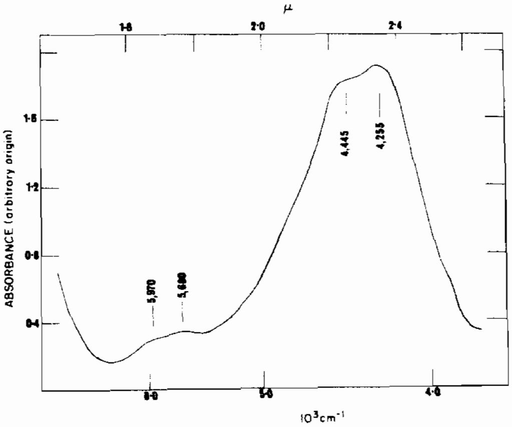

Figure 9. Sublimed film of V $Dipy_3$. Spectrum at liquid helium temperature. Detail of the first absorption band. Note the splitting of the band and the appearance of a weaker band at ~6,000 cm^{-1}.

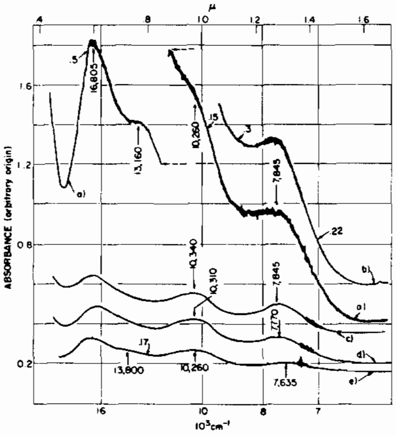

Figure 10. (a) Sublimed film of V $Dipy_3$. Room temperature. (Figure 8c continued). (b) Same, at 78°K. (Figure 8d continued). (c) Blue V $Dipy_3$ at 78°K (Figure 8d cont'd). (d) Same as (c) but at room temperature. (e) Blue THF-solution of V $Dipy_3$ at room temperature (0.2 mm against 0.2 mm THF).

The absorption spectra of Ti $Dipy_3$ are to be found in Figures 12 and 13. The first absorption band appeared at ~6,000 cm^{-1}, not as low as for V $Dipy_3$, but still at uncommonly low energy.

Cr $Dipy_3$, although possessing the same volatility of the two previous systems, had a markedly different absorption (Figures 14 to 16, and Table I).

A final observation concerning the low-temperature spectra of sublimed films should be added. The sublimator of Figure 3 was operated so as to separate on sublimation the metal dipyridyls from any free dipyridyl produced in the sublimation. Also, once the sublimed samples had been studied at room tem-

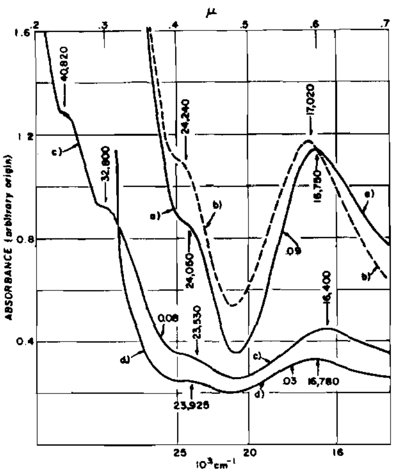

Figure 11. Blue V Dipy₃ at room temperature. (Figure 10a cont'd). (b) Same, at 78°K. (c) V Dipy₃ at room temperature. (Figure 10d cont'd). (d) THF-solution of V Dipy₃. (Figure 10e cont'd).

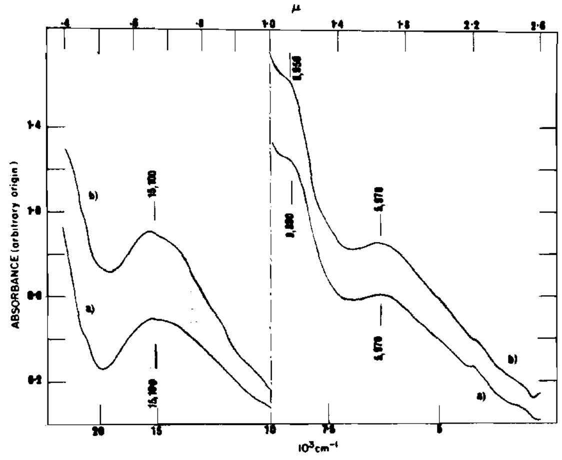

Figure 12. Sublimed film of blue Ti Dipy₃. (a) Room temperature. (b) At 78°K.

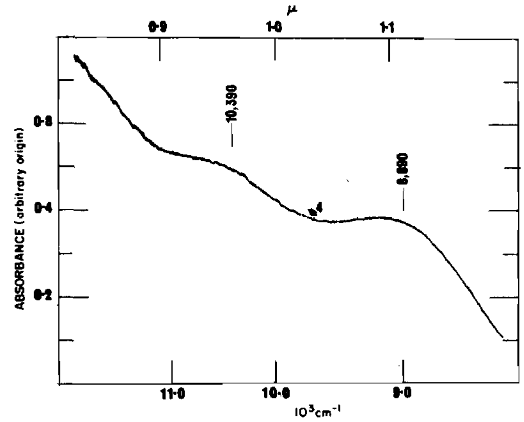

Figure 13. Sublimed film of Ti Dipy₃. Detail of the absorption at 1 μ. Room temperature.

perature, cooling of the system for low-temperature runs was carried out in a way to minimize dipyridyl condensation on the samples. Absorption edges in the near UV, appearing in some of the low-temperature spectra could be due to some dipyridyl condensation.

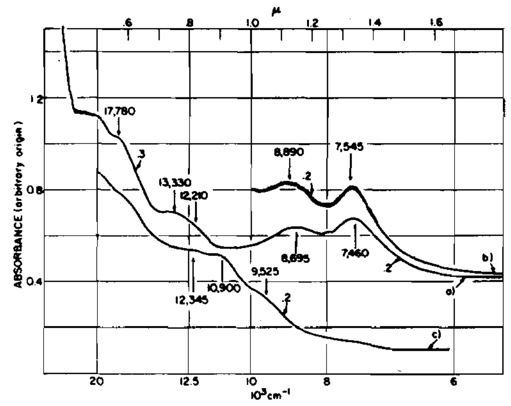

Figure 14. Sublimed film of brown Cr Dipy₃. (a) At room temperature. (b) Same, at 78°K. (c) Brown benzene extract of Cr Dipy₃: 0.05 mm against 0.05 mm benzene. (See text).

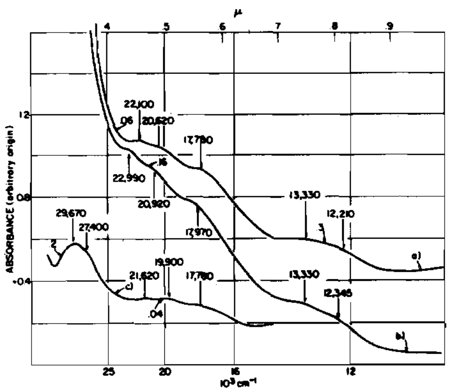

Figure 15. (Figure 14 cont'd). (a) (b) Sublimed Cr Dipy₃ at room temperature and 78°K respectively. (c) Benzene extract.

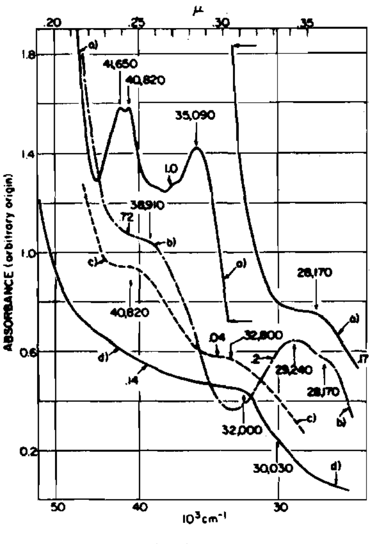

Figure 16. Comparison of absorptions in UV. Room temperature spectra. (a) Sublimed film of Ti Dipy₃. Sample from a different preparation than that of Figures 12 and 13. (b) Sublimed film of Cr Dipy₃. (Figure 15a cont'd). (c) Sublimed V Dipy₃. (Figure 11c cont'd). (d) Sublimed 2,2′-dipyridyl.

Infrared absorptions of three sublimed films are to be found in Figures 17 and 18. The absorption lines are mainly concentrated in the region from 1,500 cm^{-1}

Table I. Absorption peaks (in cm^{-1}) and their absorbance values (in optical-density units) for M $Dipy_3$ systems (M=V, Ti, Cr). Room temperature spectra

V $Dipy_3$ [a]	V $Dipy_3$ [b]	Ti Dipy [c]	Cr Dipy [d]	Cr $Dipy_3$ [e]
4 210 (0.45)		5 970 (0.6)	7 460 (0.26)	9 525 (0.22)
7 845 (0.55)	7 635 (0.05)	8 890 (1.25)	8 695 (0.22)	10 900 (0.41)
10 260 (1.05)	10 260 (0.12)	10 390 (1.35)	12 210 (0.23)	12 345 (0.43)
13 160 (1.5)	13 800 [f]	15 100 (1.65)	13 330 (0.28)	17 780
16 805 (1.9)	16 780 (0.18)		17 780 (0.62)	19 900
23 700 (1.7)	23 925 (0.10)	22 860	20 620 (0.72)	21 620
31 500 (3.7)		27 590 (2.2)	22 100 (0.74)	27 400
		33 330 (2.55)	28 170 (1.45)	29 670
			29 240 (1.53)	
			38 910 (2.15)	

[a] Sublimed film. [b] THF solution. [c] Sublimed film. [d] Sublimed film. [e] Benzene extract (see text). [f] Shoulder.

to 600 cm^{-1}. The spectra of Figure 17 show marked differences from the absorption of dipyridyl.

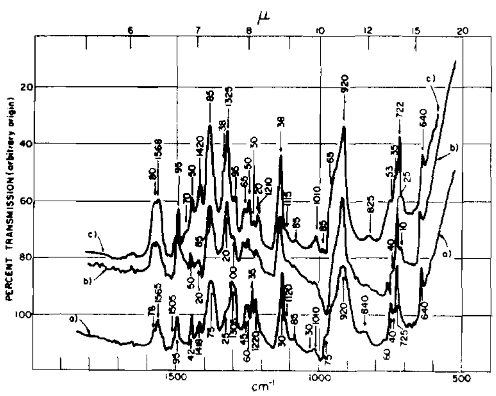

Figure 17. Infrared spectra in the sodium chloride region. (a) Sublimed film of blue V $Dipy_3$. Same sample and configuration as Figures 8a, 9d, 10c. (b) Sublimed film of Ti $Dipy_3$. Same sample and configuration as Figures 11a,b, 12a,b, 13a. (c) Sublimed film of Ti $Dipy_3$ from a different preparation.

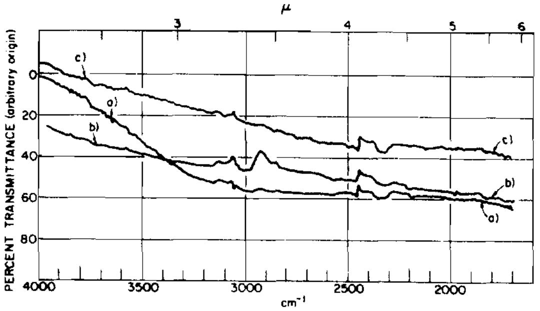

Figure 18. (Figure 17 cont'd). Note for (a) the absorption band with threshold at 3,200 cm^{-1}.

Yb $Dipy_3$. A very intense band peaking at 0.85 μ was found to have a molar absorptivity of the order of 10^5 (Figure 19). Two more bands of comparable intensity were found in the visible region (Figure 20). Accordingly 1 mm solutions of Yb $Dipy_3$, 1 m*M* in Yb were found to be practically opaque down to 2 μ.

The absorption of the Tm analogue was greatly similar to that of Yb $Dipy_3$, both in the near infrared and in the visible. Also, in spite of the difference in

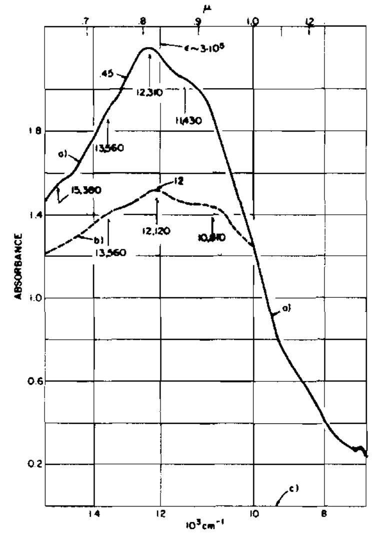

Figure 19. (a) Brown THF-solution of Yb $Dipy_3$ (from Yb and dipyridyl in liquid ammonia). 0.05 mm Solution against air. Room temperature. (b) Brown THF solution of the analogous Tm dipyridyl complex. 0.2 mm against 0.2 mm THF. Room temperature. (c) Zero line for (a).

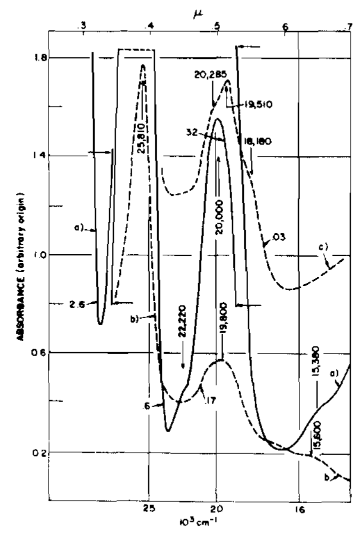

Figure 20. (a) Brown THF-solution of Yb $Dipy_3$. (Figure 19a cont'd. (b) Same as (a), but for a less absorbing sample. (c) Brown Tm solution. (Figure 19b cont'd).

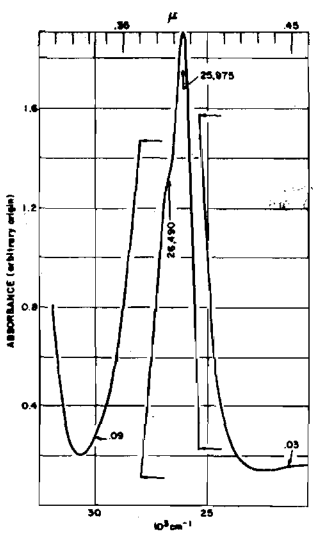

Figure 21. Brown Tm solution. (Figure 20c cont'd).

colour, Li Dipy, Yb $Dipy_3$, and its Tm analogue appeared to have a similar pattern of absorption, although the structure of the band in the near infrared is less clearly defined for the two latter systems. No indication of typical lines of trivalent Yb or Tm were found in the spectra of either systems.

Conclusion

The very intense absorption bands in the visible and in the near infrared for Yb $Dipy_3$, and the analogous complexes of the other lanthanides, are going to make it very difficult to detect the presence, if any, of the absorption lines of trivalent lanthanides. The latter absorptions in effect have molar-absorptivity values ranging from 1 to 10. For a system with enough lanthanide present for the detection of $4f^n$ lines, the broad absorption bands of the complex will make the system practically opaque. So it appears that a spectroscopic detection of any reduction of the lanthanide ion in these complexes is going to be very difficult.

On the other hand, all of the lanthanide dipyridyl complexes we prepared, before completely decaying to weakly coloured decomposition products in THF, consistently went through an intermediate decomposition phase, characterized by blue THF solutions. These blue THF solutions did not appreciably absorb in the near infrared. This property could make them useful for the purpose of a spectroscopic detection of lanthanide reduction. Absorption peaks of some of these phases are given in Table II.

It is interesting that the complexes of Li (that is Li Dipy); Yb and Tm discussed above should have a similar pattern of absorption, in spite of the difference in colour on visual inspection. The similarity implies that in these systems the central ion is not very important to the effect of the optical absorption and that the reduction process mainly affects the dipyridyl ligand. In the case of V, Ti, and Cr, as one can conclude from the observed spectra, a different central ion produces different absorption patterns. This implies a stronger metal-ligand interaction, in line with a typical transition-series behaviour. Other systems should be quite interesting for possible intermediate behaviour, for instance green U $Dipy_4$ or violet Si $Dipy_3$.[1] Even the present results on a few only of the known neutral dipyridyl complexes show that spectroscopic studies will be important in clarifying the bewildering complexity in the field of these unusual compounds.

Table II. Absorption peaks (in cm^{-1}) and absorbance values (in optical-density units) of intermediate and decomposition phases (see text)

Sm [a]	11,270 (0.2)	12,500 (0.30)	16,200 (4.)		
Yb [b]		15,680 (0.45)	17,300 (0.65)	21,620 (0.4)	24,240 (0.6)
U [c]		15,260 (0.5)	17,180 (0.75)	22,470 (0.6)	

[a] Intermediate olive-green phase from $SmCl_3 + 3Dipy + Li Dipy$ in THF. [b] Blue decomposition phase from Yb (met) + Dipy in THF. Spectrum at 78°K. [c] Blue-green decomposition phase from $UCl_6 + Dipy + Li_2Dipy$ in benzene.

Finall, if in the neutral dipyridyl complexes the lanthanide ion is not reduced, then in these systems the $4f^n$ ions will be coordinated to ligands possessing an unpaired electron, with its associated magnetic moment. This situation is probably unique amongst rare-earths compounds. One can accordingly expect very pronounced magnetic interactions of the $4f^n$ ion with the magnetic moment of the ligands.

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