absent. The linear nature of this relationship predicts that Gd(NOTA) should be less stable than Gd(EDTA)$^-$.

DOTA is a octadentate chelate like DTPA. Although DOTA has one less oxygen donor atom than DTPA, the Ln(DOTA)$^-$ complexes are all more stable than the corresponding Ln(DTPA)$^{2-}$ complexes. This is precisely what one would predict from the $\sum pK_a$ values for the two chelates. The log K value predicted for Gd(DOTA)$^-$ from the correlation shown in Figure 2 is within 5% of our measured value. Loncin et al.[22] have recently reported log K values for Eu(DOTA)$^-$ and Tb(DOTA)$^-$ (28.2 and 28.6, respectively) as determined by a gravimetric technique. Our measurements indicate that these values are about 3 orders of magnitude too high.

The solid-state structure of Eu(DOTA)$^-$ indicates that the chelate is strained, resulting in variable Eu–N bond lengths.[23] This suggests that the Eu^{3+} cation is too large to fit into the lowest energy [3333] square conformation of the tetraazadodecane ring, and hence the complex is slightly distorted. A NMR study[13] has shown that La(DOTA)$^-$, Pr(DOTA)$^-$, and Eu(DOTA)$^-$ have similar free energies of activation for ethylenediamine proton interconversion between two staggered conformations. Our results indicate that these three ions are too large to satisfy the stereochemical requirements of the tetraazadodecane ring and, although these complexes are quite rigid on the NMR time scale at room temperature, they are considerably more flexible than the complexes formed by the heavier cations,[13] i.e., Yb(DOTA)$^-$ and Lu(DOTA)$^-$. The sharp increase in log K we observe between Eu(DOTA)$^-$ and Gd(DOTA)$^-$ may reflect a more precise cation size requirement of the chelate. The nearly constant log K values found for Gd^{3+}–Tm^{3+} complexes with DOTA indicate that ion size is not a critical determinant of stability once a cation of favorable size, i.e., Gd^{3+}, has been presented to the chelate. It is not until the charge denstiy on the cation greatly increases does the stability of the complex begin to increase again, as in the case of Yb(DOTA)$^-$ and Lu(DOTA)$^-$.

Acknowledgment. This work was supported in part by grants from the Robert A. Welch Foundation (No. AT-584) and Mallinckrodt Inc. and by Biomedical Sciences Support Grant S07RR-07133 from the Division of Research Resources, NIH.

Registry No. NOTA, 56491-86-2; DOTA, 60239-18-1; La, 7439-91-0; Ce, 7440-45-1; Pr, 7440-10-0; Nd, 7440-00-8; Sm, 7440-19-9; Eu, 7440-53-1; Gd, 7440-54-2; Tb, 7440-27-9; Dy, 7429-91-6; Ho, 7440-60-0; Er, 7440-52-0; Tm, 7440-30-4; Yb, 7440-64-4; Lu, 7439-94-3.

---

(22) Loncin, M. F.; Desreux, J. F.; Merciny, E. *Inorg. Chem.* **1986**, *25*, 2646.

(23) Spirlet, M. R.; Rebizant, J.; Desreux, J. F.; Loncin, M. F. *Inorg. Chem.* **1984**, *23*, 359.

Contribution from the Laboratory
of Inorganic and Analytical Chemistry,
University of Leuven, 3030 Heverlee, Belgium

Luminescence from and Absorption by the $^3T_{1g}$ Level of the Hexacyanocobaltate(III) Ion

L. Viaene and J. D'Olieslager*

Received September 24, 1986

The properties of the $^3T_{1g}$ level of the hexacyanocobaltate(III) ion and its importance in the photochemistry of the ion have been extensively investigated.[1] All photochemical activity of Co(CN)$_6^{3-}$ is believed to originate from this level.

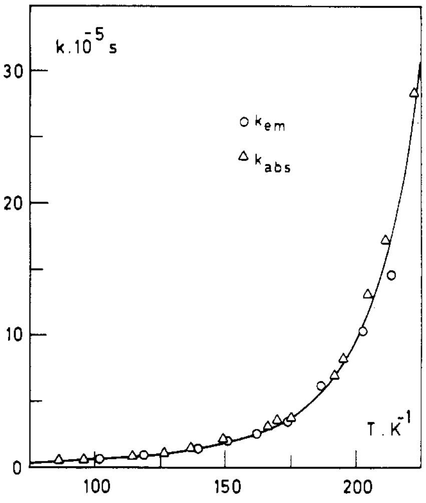

Figure 1. First-order decay rate constants as a function of temperature: solvent, EPA; k_{abs}: absorption data; k_{em}, emission data.

The emission from the triplet state has been observed in solids,[2-4] but its intensity is strongly temperature dependent. Luminescence of Co(CN)$_6^{3-}$ in solution is extremely weak at room temperature: only by using a sampling technique and by deconvoluting the data, in order to separate the signal from the laser pulse, were Conti et al.[5] able to calculate a lifetime of 2.6 ns.

Although the triplet is usually populated via intersystem crossing from the $^1T_{1g}$ level, direct singlet–triplet absorption from the $^1A_{1g}$ ground level has been observed around 396 nm.[6,7]

We reported on the spectral features of a transient species, formed upon laser flash photolysis of the Co(CN)$_6^{3-}$ ion at 94 K, which we assumed to be the $^3T_{1g}$ triplet state.[8] We present now experimental evidence that the luminescence, observed earlier,[2-4] and the transient spectrum measured by us related indeed to the same species. The kinetic behavior as a function of temperature is indeed the same for the absorbing and the emitting entity.

Experimental Section

The experimental set up for transient absorption measurements was identical with the one used earlier.[8] Samples of (TBA)$_3$Co(CN)$_6$ were either dissolved in EPA (ethanol–isopentane–ethyl ether) or in ethylene glycol–water mixtures (60/40 vol. %). The spectrophotometric cell was suspended in an all-quartz Dewar and cooled by means of a thermostated stream of cold nitrogen gas. For the observation of the luminescence an additional Jobin Yvon H20-IR monochromator was mounted at 90° relative to the exciting beam. In order to minimize the interference of the laser pulse, special precautions were required: the fundamental component of the ruby laser light (694 nm) was removed by means of a CuSO$_4$ solution with a path length of 10 cm. The 347-nm component was prevented from entering the monochromator by means of a suitable glass filter.

The emission spectra were corrected for the variations in sensitivity of the detection system by using the emission data of a tungsten lamp with known spectral distribution.

A second correction factor is required in order to take into account the variation of the absorption at the wavelength of the laser, when the samples are cooled. When the sample is cooled from 293 to 110 K the absorbance at 347 nm of [(n-C$_4$H$_9$)$_4$N]$_3$Co(CN)$_6$ decreases by a factor of 5! Presumably the important decrease is due to a combination of the band being vibronic and the laser exciting into the low-energy edge.

Photosolvation quantum yields at low temperature were measured by using the same Dewar setup. The irradiation was performed with the 313-nm line of a high-pressure mercury arc, whose light output was monitored with a chemical actinometer. The amount of light incident

---

(1) Zinato, E. In *Concepts of Inorganic Photochemistry*; Adamson, A., Fleischauer, P. D., Eds.; Wiley-Interscience: New York, 1975; Chapter 4.

(2) Mingardi, M.; Porter, G. B. *J. Chem. Phys.* **1966**, *44*, 4354.

(3) Kirk, D.; Ludi, A.; Schläfer, H. *Ber. Bunsen-Ges Phys. Chem.* **1969**, *73*, 669–683.

(4) Kataoka, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2078–2086.

(5) Conti, C.; Castelli, F.; Forster, L. S. *J. Phys. Chem.* **1979**, *83*, 2371–2376.

(6) Fujita, J.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1963**, *36*, 1281–1285.

(7) Loeb, B.; Zuloaga, F. *J. Phys. Chem.* **1977**, *81*, 59–63.

(8) Viaene, L.; D'Olieslager, J.; Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1979**, *101*, 1405–1409.

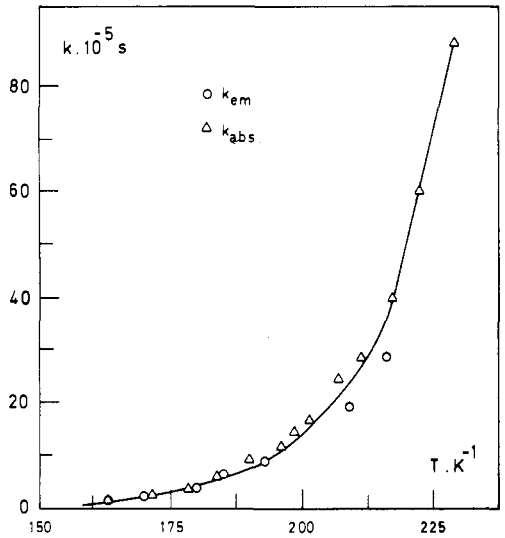

Figure 2. First-order decay rate constants as a function of temperature: solvent, ethylene glycol–water; $k_{\rm abs}$, absorption data; $k_{\rm em}$, emission data.

upon the reaction vessel was calculated by using the photoaquation reaction of $Co(CN)_6^{3-}$ in water as a reference. The quantum yield of this reaction is known to be 0.31.[9]

The amount of $Co(CN)_5H_2O^{2-}$ produced was determined spectrophotometrically.

Results

We measured the transient absorption of $[(n\text{-}C_4H_9)_4N]_3Co(CN)_6$ as a function of time in two glass matrices: EPA and ethylene glycol–water. The spectrum obtained in the last solvent was identical with the one reported earlier in EPA.[8] The transient signals were found to decay according to a first-order process, and k_1 values were obtained from ln A vs. time plots. In Figures 1 and 2 we collected the k_1 values as a function of temperature in the two different matrices. If this transient spectrum is due to the absorption of the $^3T_{1g}$ state, its triplet emission should be observable in the same experimental conditions. This is indeed the case: a weak, but readily observable band is found, with a maximum at 726 nm in ethylene glycol–water (165 K) and at 755 nm in EPA (105 K). The spectra were obtained by recording the transient luminescence at different wavelengths and extrapolating the ln I vs. time plots to $t = 0$. Attempts to measure the spectrum with a conventional spectrofluorometer were unsuccessful, due to the low sensitivity of the apparatus at these wavelengths and to the low intensity of the signal.

The maximum of the emission shifts slightly to higher wavelengths at higher temperatures.

The luminescence decays according to first-order kinetics. In Figures 1 and 2 we superimposed the luminescence as a function of temperature upon the results for the absorption rate constants. The coincidence is perfect. Around 220–230 K the k values can no longer be measured with our setup: the duration of the laser flash is about 30 ns, and from this temperature on the stray light from the laser interferes with the absorption and the emission measurements.

At the same temperature, the photosolvation becomes observable and gains more importance as the temperature rises. This is demonstrated in Figure 3 where the photosolvolysis quantum yield in ethylene glycol–water as solvent is plotted as a function of temperature. The value of 0.17 at 293 K corresponds reasonably well with the value 0.14 for the same solvent.[10]

Discussion

The experimental results demonstrate the existence of a weak luminescence from the triplet state of $Co(CN)_6^{3-}$ in EPA and ethylene glycol–water solutions. In order to make it observable the competing solvation has to be inhibited by a decrease of the temperature. The position of the maximum of the triplet luminescence depends strongly on the environment of the $Co(CN)_6^{3-}$ center. Even in pure or mixed crystals the position of the maximum varies from 637–680[4] to 700[2,3] or 713 nm[7]. Since most of these spectra were recorded without correction for the dependence of the sensitivity on the wavelength, some doubt arises on the actual accuracy of the position of the maximum.

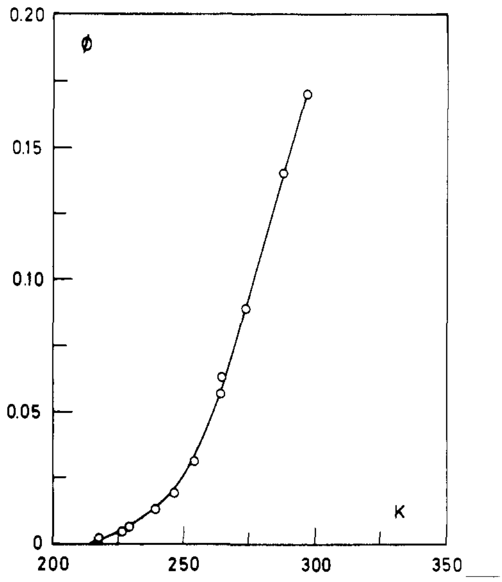

Figure 3. Photosolvation quantum yield as a function of temperature for $[(n\text{-}C_4H_9)_4N]_3Co(CN)_6$ in ethylene glycol–water.

It is clear from Figures 1 and 2 that the excited-state absorption spectrum published earlier[8] belongs indeed to the triplet state: in both solvents the two signals decay with a same rate constant, at any temperature. The population of the triplet at $t = 0$ is almost constant in the investigated temperature area. This suggests that the efficiency for the population of the triplet—the intersystem crossing from the singlet $^1T_{1g}$ level—is not dependent on temperature.

About the actual value of $\Phi_{\rm ISC}$ conflicting data were published. While sensitization experiments with biacetyl gave a value of 0.4,[11] Ford found a value of 0.9 by direct excitation into the triplet level.[12] We have reasons to believe that $\Phi_{\rm ISC}$ is indeed 1[13] independent of the temperature.

The actual photosolvolysis reaction on the other hand is temperature dependent, as shown in Figure 3. This is in full agreement with a cage recombination mechanism, in which a CN^- ligand needs some kinetic energy in order to escape from the solvent cage.

The decay of the triplet in the low-temperature glasses (the k values of Figures 1 and 2) is controlled by several processes: when ln k is plotted vs. $1/T$ no linear relationship is found. Thus not only the solvation reaction but the different radiationless deactivation processes will depend on the temperature.

It is striking that in ethylene glycol–water mixtures the luminescence at 165 K is 50% more intense than that in EPA at the same temperature. The deactivation constant at this temperature is correspondingly lower (1.5×10^5 s^{-1} vs. 2.9×10^5 s^{-1}). The rate constant is however more temperature dependent in ethylene glycol–water than in EPA.

Conclusions

We proved irrefutably that the triplet state of $Co(CN)_6^{3-}$, known from its luminescence in the solid state, is indeed the species responsible for the transient absorption observed at low temperature.

---

(9) Moggi, L.; Boletta, F.; Balzani, V.; Scandola, F. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2589–2597.

(10) Scandola, F.; Scandola, M. A.; Bartocci, C. *J. Am. Chem. Soc.* **1975**, *97*, 4757–4758.

(11) Scandola, M. A.; Scandola, F. *J. Am. Chem. Soc.* **1972**, *94*, 1805–1810.

(12) Nishazawa M.; Ford P. C. *Inorg. Chem.* **1981**, *20*, 294–295.

(13) (a) Claes, R. Doctoral Thesis, Leuven, 1986. (b) Sensitization experiments with xanthone: Claes, R.; D'Olieslager, J., results to be submitted for publication.

At higher temperatures, the photosolvation and the other deactivation reactions become so fast that the luminescence and the absorption of the triplet are no longer observable.

Registry No. $[(n\text{-}C_4H_9)_4N]_3Co(CN)_6$, 20792-39-6; $[(n\text{-}C_4H_9)_4N]\text{-}Co(CN)_5H_2O$, 106800-13-9.

Contribution from the Institute of Inorganic
and Analytical Chemistry, University of Fribourg,
CH-1700 Fribourg, Switzerland

Stability of d^3 Diimine Complexes: Molybdenum(III) vs. Chromium(III)

Christine Cornioley-Deuschel and Alex von Zelewsky*

Received September 16, 1986

The number of well-characterized complexes of Cr(III) has increased enormously since the early days of coordination chemistry, when they already played an important part in the development of new theories.[1] On the other hand, coordination compounds of Mo(III) have not been studied in great detail, except some complexes, especially the aquo ions[2] and species like Mo(edta)$^-$.[3] This striking difference between elements of the same transition-metal group has been generally attributed[4] to an instability of Mo(III) and W(III) compared to that of higher oxidation states. It was often assumed that Mo(III) and W(III) would be as inert as Cr(III) owing to their d^3 configuration.[5]

In view of the capability of the chelate ligand 2,2′-bipyridine (bpy) to act as a relatively strong π acceptor and thus stabilize low oxidation states as e.g. in $Ru(bpy)_3^{2+}$, we attempted to study the properties of $Mo(bpy)_3^{3+}$.

This complex has been reported to exist in the compounds $Mo(bpy)_3X_3$ ($X = I^-, Br^-, Cl^-$),[6,7] but more recent results raise doubts about the existence of these compounds.[8]

Among the few tris-bidentate mononuclear Mo(III) complexes described in the literature, the work of Ghosh and Prasad[9] is noteworthy. These authors prepared tris complexes of several bidentate ligands, including ethylenediamine (en) and 2-(2-pyridyl)benzimidazole, from $(NH_4)_2MoCl_5(H_2O)$. We report here the synthesis of $Mo(bpy)_3(PF_6)_3$ from the same starting material. ^2H NMR of complexes containing deuteriated ligands[10,11] is used to study the species in solution.

Experimental Section

General Considerations. Chemicals were purchased from Fluka or Aldrich. Methanol was distilled over Mg. bpy was recrystallized from hexane. $(NH_4)_2MoCl_5(H_2O)$ was prepared by the procedure of F. A. Cotton.[12] All manipulations were carried out under N_2 with use of Schlenk apparatus.

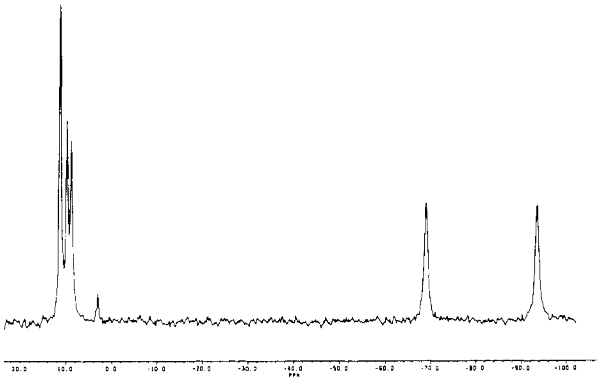

Figure 1. ^2H NMR spectrum of "$Mo(bpy\text{-}6,6'\text{-}d_2)_3^{3+}$" in acetone.

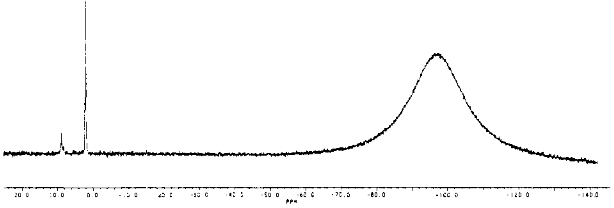

Figure 2. ^2H NMR spectrum of $Cr(bpy\text{-}6,6'\text{-}d_2)_3^{3+}$ in acetone.

Table I. Electrochemical Data for Molybdenum Complexes with 2,2′-Bipyridine

	half-wave potentials vs. SCE, V[a]				
	IV/III	III/II	II/I	I/0	ref
$Mo(bpy)_3^{3+}$	1.00[b]	−0.58	−1.05		this work
$Mo(bpy)_3$		−0.01[b]	−0.42	−1.13	17
$Mo(bpy)_2Cl_2^+$	0.92[b]	−0.63[c]	−1.08[c]		17

[a] All values obtained at a rotating platinum electrode unless noted otherwise. [b] Irreversible anodic process. [7] Values obtained at a dropping mercury electrode.

Measurements. Cyclic voltammetry: Metrohm Polarecord, Model E 506; VA scanner, Model E 612; X-Y printer, Model MP 704 4A; platinum-disk electrode, platinum auxiliary electrode, $Ag/AgNO_3$ reference electrode; supporting electrolyte tetra-*n*-butylammonium perchlorate. ^2H NMR: Bruker AM 360 spectrometer; sealed tubes. Magnetic susceptibility: Bruker BMNS 50/50 1S/BE10, Faraday method; room temperature on powdered samples; calibration with $HgCo(NCS)_4$.

Synthesis. $Mo(bpy)_3(PF_6)_3$ was obtained by mixing 2 mmol of $(NH_4)_2MoCl_5(H_2O)$ with 3 equiv of bpy in 100 mL of dry methanol for 5 h at room temperature. After filtration of the reaction mixture the complex was precipitated by adding an excess of NH_4PF_6 in methanol. The solid was recrystallized from acetone/ether; 540 mg of a violet microcrystalline product was collected. Anal. Calcd for $C_{30}H_{24}F_{18}MoN_6P_3$: C, 36.01; H, 2.41; N, 8.41. Found: C, 37.75; H, 2.71; N, 9.00. $\mu_{eff} = 3.54\ \mu_B$.

Bpy-*6,6′-d*$_2$ was obtained by treating 6,6′-Li_2-bpy[13] in ether at −90 °C with an excess of CH_3OD. After hydrolysis and isolation of the solid, the crude product was purified by chromatography (alumina, ether/hexane 1:1).

$Cr(bpy)_3(PF_6)_3$[14] and $Cr(bpy)_2(DMF)_2(PF_6)_3$[15] were prepared by published methods.

Results

An examination of the ^2H NMR spectrum of $Mo(bpy\text{-}6,6'\text{-}d_2)_3(PF_6)_3$ in acetone (Figure 1) shows two resonances of equal intensity at −94 and −69 ppm, corresponding to deuterons of bpy-*6,6′-d*$_2$ bound to a paramagnetic Mo(III), thus indicating the existence of two sets of equivalent deuterons. In the diamagnetic region the spectrum exhibits one resonance at 8 ppm corresponding

---

(1) Werner, A. *Neue Anschauungen auf dem Gebiete der Anorganischen Chemie*, 3rd ed., Vieweg & Sohn: Braunschweig, West Germany 1913.

(2) Richens, D. T.; Skykes, A. G. *Comments Inorg. Chem.* **1981**, *1*, 141.

(3) Kneale, G. G.; Geddes, A. J.; Sasaki, Y.; Shibahara, T.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1975**, 356.

(4) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

(5) Basolo, F.; Pearson, R. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1968.

(6) Steele, M. C. *Aust. J. Chem.* **1957**, *10*, 489.

(7) Carmichael, W. M.; Edwards, D. A.; Walton, R. A. *J. Chem. Soc. A* **1966**, 97.

(8) Morita, T. S.; Sasaki, Y.; Saito, K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2678.

(9) Ghosh, S. P.; Prasad, K. M. *Proceedings of the First International Conference on the Chemistry and Uses of Molybdenum*; Mitchell, P. C. H., Ed.; Climax Molybdenum Co.: Ann Arbor, MI, 1974.

(10) Wheeler, W. D.; Kaizaki, S.; Legg, J. I. *Inorg. Chem.* **1982**, *21*, 3248.

(11) Everett, G. W.; Johnson, A. *J. Am. Chem. Soc.* **1972**, *94*, 1419.

(12) Cotton, F. A.; Brencic, J. V. *Inorg. Synth.* **1972**, *13*, 171.

(13) Parks, J. E.; Wagner, B. E.; Holm, R. H. *J. Organomet. Chem.* **1973**, *56*, 53.

(14) Kane-Maguire, N. A. P.; Hallock, J. S. *Inorg. Chem. Acta* **1979**, *35*, L309-11.

(15) Porter, G. B.; Van Houten, J. *Inorg. Chem.* **1979**, *18*, 2053.

0020-1669/87/1326-0962$01.50/0