

Short Communications

Photoluminescence of Tricyanomethanide

(Received June 15, 1992)

Carbanion / Luminescence

Tricyanomethanide shows a fluorescence ($\lambda_{\max} = 418$ nm) and a phosphorescence ($\lambda_{\max} = 470$ nm, $\tau = 0.85$ s) which is observed only at 77 K. It is suggested that the Stokes shift of the fluorescence ($\Delta\bar{\nu} = 12050$ cm⁻¹) is caused by a Jahn-Teller distortion in the $\pi\sigma^*$ excited state.

Tricyanomethanid zeigt eine Fluoreszenz ($\lambda_{\max} = 418$ nm) und eine Phosphoreszenz ($\lambda_{\max} = 470$ nm, $\tau = 0.85$ s), die nur bei 77 K beobachtet wird. Es wird vorgeschlagen, daß die Stokessche Verschiebung der Fluoreszenz ($\Delta\bar{\nu} = 12050$ cm⁻¹) durch eine Jahn-Teller-Verzerrung im angeregten $\pi\sigma^*$ -Zustand hervorgerufen wird.

Tricyanomethanide is one of the few carbanions which are stable under ambient conditions. However, while the electronic structure and the absorption spectrum of this anion have been studied [1–3], electronically excited $C(CN)_3^-$ has not yet been characterized. Recently, we investigated the photophysics of $M^+Cl_3^-$ ($M = Ge, Sn$ and Pb) [4] which is isoelectronic with carbanions. In terms of coordination compounds and in analogy to the complex ions MCl_3^- the tricyanomethanide can be considered to consist of three cyanide ligands which are coordinated to a central C^{2+} cation with an s^2 electron configuration. This analogy stimulated the study of the photophysical properties of $C(CN)_3^-$.

The absorption ($\lambda_{\max} = 278$ nm, $\epsilon = 230$; $\lambda_{\max} = 238$ nm, $\epsilon = 1800$; $\lambda_{\max} = 211$ nm, $\epsilon = 37000$) and emission spectra of $C(CN)_3^-$ are shown in Fig. 1. The excitation spectrum matches the absorption spectrum. The luminescence consists of a short-lived fluorescence at $\lambda_{\max} = 418$ nm and a long-lived ($\tau = 0.85$ s) phosphorescence at $\lambda_{\max} = 470$ nm which was completely quenched at room temperature.

The nature of the emitting excited state can be understood on the basis of a qualitative MO scheme (Fig. 2) which includes only the σ interaction of the CC_3 moiety [5]. In the ground state $C(CN)_3^-$ has not a trigonal pyramidal but a trigonal planar (D_{3h}) structure [6] which is stabilized by π interaction. The HOMO a'' which is localized at the central carbon atom

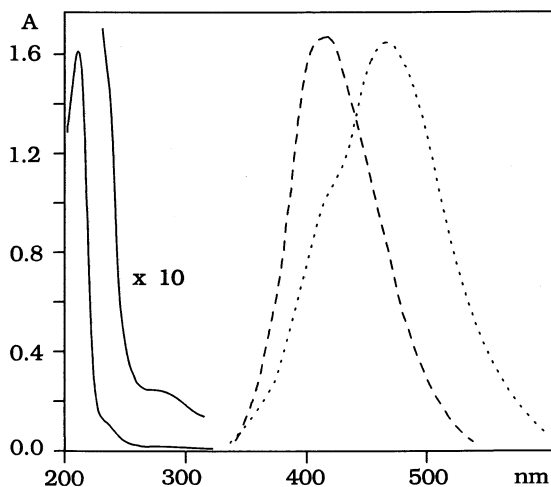


Fig. 1. Electronic spectra of $K[C(CN)_3]$. Absorption (1-cm cell): 4.32×10^{-5} M in water at r.t. (—). Emission: 2.7×10^{-3} M in water at r.t. (---) and in ethanol at 77 K (\cdots), $\lambda_{exc} = 300$ nm, intensity in arbitrary units.

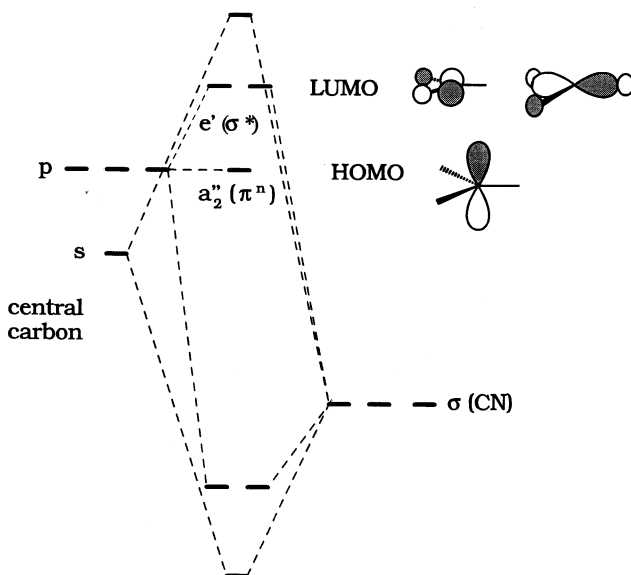
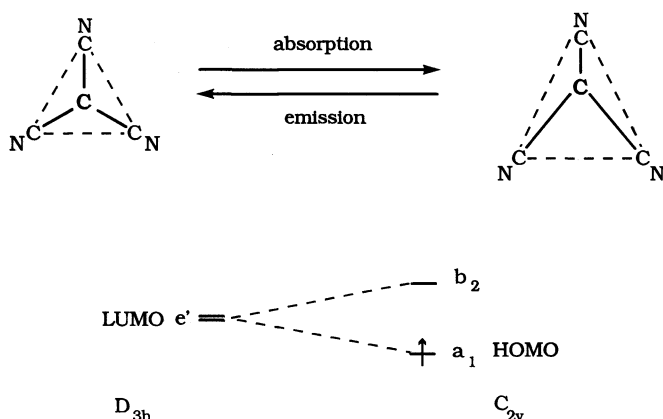


Fig. 2. Qualitative MO scheme for the σ interaction of the CC_3 moiety of $C(CN)_3^-$.

becomes bonding by overlap with the π^* orbitals of the nitrile substituents [5, p. 146]. This interaction does not change the ordering of the HOMO a_2'' and the degenerate LUMO e' [1, 2] which is σ antibonding with respect to the C–C bonds. In accordance with a previous report [2] we assign the



Scheme 1.

two longest-wavelength absorptions at $\lambda_{\max} = 278$ nm and $\lambda_{\max} = 238$ nm to the spin-allowed ${}^1A_{1g} \rightarrow {}^1E''$ ($a'' \rightarrow e'$, Fig. 2) transition, split by Jahn Teller distortion. In the excited state the degeneracy of the e' orbitals can be lifted, for example, by the equilateral triangle to isosceles ($D_{3h} \rightarrow C_{2v}$) distortion [5, p. 99] (Scheme 1). The large Stokes shift ($\Delta\bar{\nu} = 12050$ cm⁻¹) of the fluorescence seems to reflect this structural rearrangement in the excited state. The fluorescence competes with intersystem crossing to the triplet state which is characterized by the slow decay of the phosphorescence at 77 K. The singlet-triplet separation amounts to 2650 cm⁻¹.

Acknowledgment

This work was supported by the Deutsche Forschungsgemeinschaft (Grant Vo 211/8-1).

References

1. J. H. Enemark and R. H. Holm, *Inorg. Chem.* **3** (1964) 1516.
2. D. A. Dixon, J. C. Calabrese and J. S. Miller, *J. Am. Chem. Soc.* **108** (1986) 2582.
3. J. Cioslowski, S. T. Mixon and E. D. Fleischmann, *J. Am. Chem. Soc.* **113** (1991) 4751.
4. H. Nikol, A. Becht and A. Vogler, *Inorg. Chem.* **31** (1992) 3277.
5. T. A. Albright, J. K. Burdett and H.-H. Whangbo, *Orbital Interactions in Chemistry*, Wiley, York (1985)
6. J. R. Witt and D. Britton, *Acta Crystallogr.* **B 27** (1971) 1835.

Horst Kunkely and Arnd Vogler*

Institut für Anorganische Chemie, Universität Regensburg
Universitätsstrasse 31, D-8400 Regensburg, Federal Republic of Germany