Inorganica Chimica Acta, *189* (1991) 55–58

On the preparation and luminescence of *trans*- and *cis*-$[Cr(en)_2(CN)_2]^+$ ions

M. Perkovic and G. Ferraudi*
Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556 (USA)

(Received May 21, 1991)

Abstract

New and efficient routes for the preparation of the *trans* and *cis* isomers of $[Cr(en)_2(CN)_2]^+$ are reported. The luminescence spectra of these compounds are also reported and compared to those of related tetraaza macrocycles. Facile vibronic distortions of the corresponding D_{4h} and C_{2v} microsymmetries are proposed to lead to unresolved emission spectra in the family of the ethylenediamine complexes.

Introduction

Cyanoamine complexes of Cr(III) have been used extensively as probes into the behaviour of electronically excited molecules both from a photophysical [1–4] and photochemical perspective [5]. Molecules of the type *trans*-$[Cr(N)_4(CN)_2]^+$, where $(N)_4$ is any polydentate amine ligand, are of particular interest in our investigations of magnetodynamic effects on the relaxation rates of excited states in Cr(III) am(m)ines [3]. One member of this class of compounds, namely *trans*-$[Cr(en)_2(CN)_2]^+$ has proved difficult to obtain despite a published preparation [6] and several additional attempts [4, 5a, 7]. We have recently developed a convenient route to the preparation of *trans*-$[Cr(en)_2(CN)_2]^+$ which may well be a useful synthetic procedure for the preparation of *trans*-$[Cr(en)_2X_2]^{n+}$ complexes in general. It is the description of this work and some photophysical observations on both *cis*- and *trans*-$[Cr(en)_2(CN)_2]^+$ complexes that is the purpose of this communication.

Experimental

All materials were of reagent grade and used without further purification. Due to explosive potential of perchlorate salts of Cr(III) amines, yields quoted are lower limits; no effort was made to recover materials mechanically from glass frits. Tris(ethylenediamine)chromium(III) thiocyanate was prepared as described in the literature [7]. t-$[Cr(en)_2(NCS)_2]^+$ was prepared by slightly modifying the method of Bailar and co-workers [8]. A total of 500 mg of $Cr(en)_3(NCS)_3$ was added** to *c.* 50 cc of chlorobenzene in a round-bottomed flask fitted to a condenser packed with 4 Å molecular sieves. The insoluble solid was rapidly stirred as the fluid was brought to reflux. After about 15 min the initially bright yellow suspension had changed to an orange–red color at which time the hot mixture was filtered to collect the solid product. The orange powder was air dried, then recrystallized from 100 cc of water by the addition of $NaClO_4$ or NH_4NCS. The solid collected by filtration was washed in succession with EtOH and Et_2O, and was then air dried. UV–Vis [9] and IR [10] were in accord with the literature values. The yield of *trans*-$[Cr(en)_2(NCS)_2]X$, $X = ClO_4^-$ or NCS^-, was better than 90%.

trans-[Cr(en)₂(TFMS)]TFMS

One gram (2.9 mmol) of *trans*-$[Cr(en)_2(NCS)_2]NCS$ was placed in a round-bottomed flask with a gas inlet arm and placed under a stream of dry N_2. Anhydrous trifluoromethanesulfonic acid (HTFMS), 100 cc, was added and the mixture was stirred for 30 min at room temperature. The temperature was then raised to 50 °C for an additional 30 min with continued purging. Upon cooling to room temper-

---

*Author to whom correspondence should be addressed.

**As the authors of ref. 8c suggest, it is important that a trace amount of NH_4NCS be present in the solid $Cr(en)_3(NCS)_3$. Typically, this is achieved by adding a large excess of NH_4NCS during recrystallization followed by washing with aqueous NH_4NCS and air drying.

ature, the deep violet–red solution was added *very carefully* dropwise to 1.5 dm^3 of rapidly stirred, ice cold Et_2O. This mixture was then refrigerated and a pink powder sedimented out overnight. The liquid layer was decanted and another liter of ether was added with stirring to the solid material. This procedure was repeated until the ether was colorless. The solid was then collected by filtration, washed with ether and dried *in vacuo* at 50 °C. The reaction yielded 1.5 g (85%) of a slightly pink powder*. *Anal.* Calc. for $Cr(en)_2(TFMS)_3 \cdot H_2O$, $C_7H_{18}N_4O_{10}S_3F_9Cr_1$: C, 13.19; H, 2.84; N, 8.38. Found; C, 13.15; H, 2.81; N, 8.79%.

$[Cr(en)_2(CN)_2]^+$

Five hundred milligrams (0.8 mmol) of *trans*-$[Cr(en)_2(TFMS)_2]TFMS$ were added to a rapidly stirred solution of 78.9 mg (1.61 mmol) of NaCN in *c.* 5 cc of DMSO at 70 °C. The solution changed from deep red to brown–orange within 15 min. The cooled solution was mixed with 75 cc of water and sorbed onto a 25×250 mm column of Sephadex SP25 cation exchange resin. The column was washed with water to remove the residual DMSO and (presumed) $Cr(CN)_6^{3-}$. Two yellow bands were eluted with 0.5 M $LiClO_4$ at pH 6.5. Both were collected, evaporated to dryness, then redissolved in *c.* 100 cc of acetone and placed into the freezer. Within three days a fine, yellow powder was precipitated in each flask. These materials were collected by filtration, washed with cold acetone and dried. The yields of *trans* isomer (band 1) was 150 mg (0.46 mmol, 57%); the *cis* isomer was collected in a slightly smaller amount, 100 mg (0.31 mmol, 38%). Some $Cr(en)_3^{3+}$ was also recovered when the column was washed with 0.5 M $LiClO_4$ at pH 3.

UV–Vis spectra were recorded in water on a Cary 219 instrument. IR spectra were recorded as KBr pellets on a Perkin-Elmer 883 instrument. Luminescence spectra were recorded using a Princeton Instruments diode array combined with an ISA 1/3 meter spectrograph. Samples in DMSO/0.01 M HTFMS (1:1 vol./vol.) were excited at 450 nm by a Candela SLL500 dye laser. Spectra were wavelength calibrated by superposition of the resonance radiation from a (Pen-Ray) Ne spectral calibration lamp. The detector's response is flat within the spectral window. Luminescent decay profiles were measured with an Hamammatsu R955 phototube biased between −700 and −900 V terminated into 1 KΩ. The spectral region of interest was isolated using an Oriel 0.1 M monochromator. The kinetic traces were recorded by a Biomation model 805 waveform recorder. Individual traces were transferred to a PC/AT computer and averaged. Kinetic fits were performed using the KINFIT package from OLIS, Jefferson, GA.

Results and discussion

Although this is not the first report of the preparation of t-$[Cr(en)_2(CN)_2]^+$, the previously published methods [5a, 6] have resulted in the recovery of little, if any, *trans* product. The *cis* and *trans* isomers prepared in this work exhibited UV–Vis spectra only slightly different from those previously reported [6, 7] and Cr–N IR bands agreed with published [6] and predicted [10] values, Fig. 1. Previous synthetic difficulties in obtaining the *trans* isomer may be largely due to the relative inertness of Cr(III) toward ligand substitution. Thus, in the presence of the basic cyanide ion, loss of the diamine ligand compete with the nucleophilic substitution of cyanide with bromo [5] or chloro [7] substituents, both of which are 'good' ligands on Cr(III). Trifluoromethanesulfonate, on the other hand, does not have a strong affinity for chromium(III). Our ob-

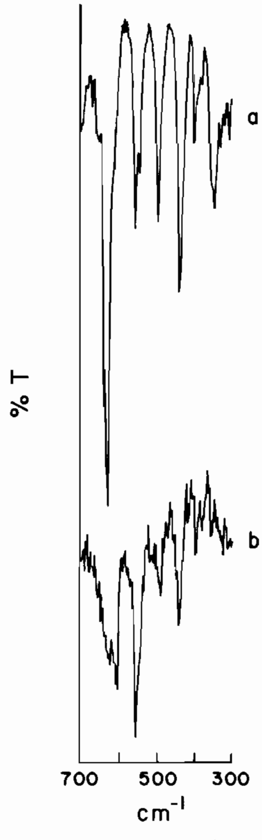

Fig. 1. Characteristic M–L IR bands of *trans*-$Cr(en)_2(CN)_2ClO_4$ (a) and *cis*-$[Cr(en)_2(CN)_2]ClO_4$ (b).

---

*The perceived color depends largely on the particle size distribution within the solid and may vary from light pink to chalky purple.

servation of multiple products ranging from $Cr(CN)_6^{3-}$ to $Cr(en)_3^{3+}$ suggests that this kinetic advantage is largely responsible for the recovery of a substantial quantity of *trans* product despite the proposed thermodynamic preference to *cis* product formation [7].

A published procedure for the preparation of *trans*-$[Cr(en)_2(NCS)_2]^+$ involves heating $Cr(en)_3(NCS)_3$ in an oven at a precisely controlled temperature. We have chosen to replace the oven with a solvent with a proper boiling point in which the starting materials and product are insoluble. This allowed for much easier temperature control and material handling while maintaining the solid state reaction conditions. Such a method substantially increased product yields and reduced the reaction time. Our attempts to prepare *trans*-$[Cr(en)_2(CN)_2]^+$ by the solid state reaction with $Cr(en)_3(CN)_3$ in the presence of NH_4NCS or NH_4NO_3 in trace amounts resulted in the recovery of only starting materials. It is possible that the preparation of *trans*-$[Cr(en)_2(CN)_2]^+$ may require a different temperature as is the case of the *cis*-$[Cr(en)_2Cl_2]^+$ synthesis [8].

The emission spectra at room temperature and at 77 K of *cis*- and *trans*-$[Cr(en)_2(CN)_2]^+$ are featureless and similar in shape (Figs. 2 and 3) and the 77 K emission lifetimes agree with literature reports [4]. The low temperature behaviour is somewhat surprising for chromium(III) amines because differences in Cr(III) microsymmetry, D_{4h} and C_{2v} for the *trans* and *cis* isomers, respectively, should be manifested in very different emission band intensity profiles. For example, on expects the centric *trans* isomer to have a relatively weak O–O band and a fairly well resolved vibronic structure. The non-centric *cis* isomer, on the other hand, should have an emission spectrum that is dominated by an intense O–O transition with little structure. In spite of this, the 77 K glassy solution spectra of both isomers are remarkably similar: both feature a relatively intense O–O transition with smaller contributions from vibronic components. While the 77 K emission spectrum of the *trans*-$[Cr(en)_2(NCS)_2]^+$ complex is even more featureless than its cyano analogue, Fig. 4, they are all similar to the 77 K spectrum of $Cr(en)_3^{3+}$ in that they are dominated by the electronic origin and with little vibronic structure. The absence of vibronic structure in the spectra of the ethylenediamine complexes stands in contrast to a rich one in the spectra of related *trans*-tetraaza macrocycles [2]. It is possible that a nuclear displacement in the excited state blurs the differences between *cis* and *trans* geometries in the en family.

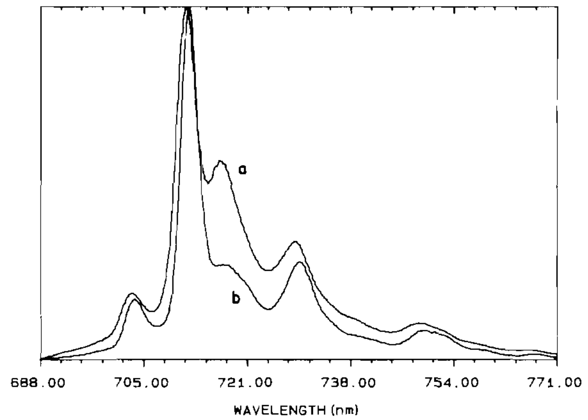

Fig. 2. Phosphorescence spectra at 77 K of *trans*- (a) and *cis*-$[Cr(en)_2(CN)_2]ClO_4$ (b) in DMSO/HTFMS glassy solution.

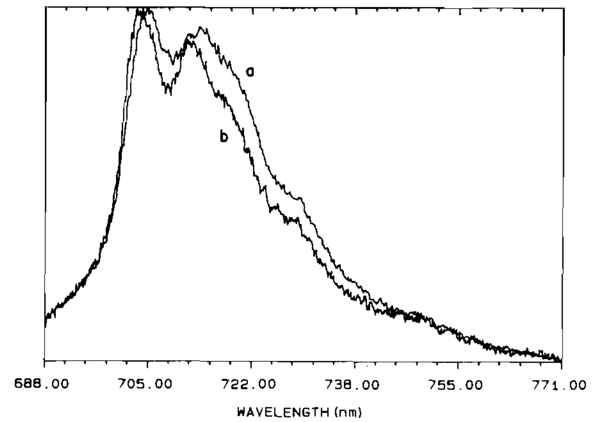

Fig. 3. Phosphorescence spectra at 300 K of *trans*- (a) and *cis*-$[Cr(en)_2(CN)_2]ClO_4$ (b) in DMSO/HTFMS solution.

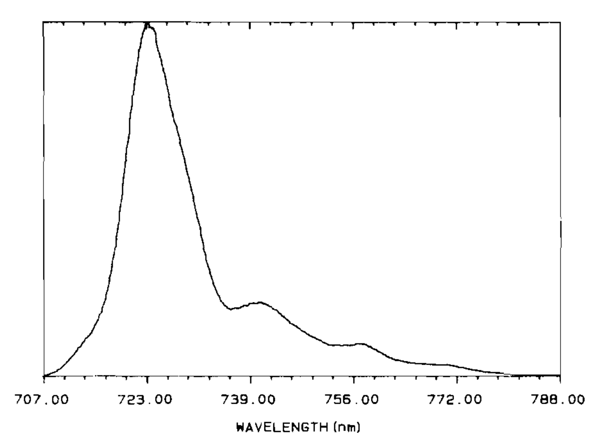

Fig. 4. Phosphorescence spectrum at 77 K of *trans*-$[Cr(en)_2(NCS)_2]NCS$ in DMSO/HTFMS solution.

Acknowledgements

The work described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Contribution No. NDRL-3377 from the Notre Dame Radiation Laboratory.

References

1 L. S. Forster, *Chem. Rev. 90* (1990) 331.
2 S. Ronco, M. W. Perkovic, M. Cozzi and G. J. Ferraudi, *Chem. Phys.,* (1992) in press.
3 M. W. Perkovic, J. Heeg and J. F. Endicott, *Inorg. Chem., 31* (1991) 3140.
4 N. A. P. Kane-McGuire, W. S. Crippen and P. K. Miller, *Inorg. Chem., 22* (1983) 696.
5 (a) A. D. Kirk and G. B. Porter, *Inorg. Chem., 19* (1980) 445; (b) P. Riccieri and E. Zinato, *Inorg. Chem., 20* (1981) 3722.
6 S. Kaizaki, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Jpn., 48* (1975) 902.
7 C. L. Rollinson and J. C. Bailar, *Inorg. Synth., 2* (1946) 196.
8 (a) C. L. Rollinson and J. C. Bailar, *Inorg. Synth., 2* (1946) 202; (b) T. D. O'Brien and J. C. Bailar, *J. Am. Chem. Soc., 67* (1945) 1856; (c) C. L. Rollinson and J. C. Bailar, *J. Am. Chem. Soc., 66* (1944) 641.
9 W. A. Baker and M. G. Phillips, *Inog. Chem., 6* (1966) 1042.
10 M. N. Hughes and W. R. McWhinnie, *J. Chem. Soc. A* (1967) 593.