Inorganica Chimica Acta, 22 (1977) L11–L13
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Reversible Intermolecular Energy Transfer between Chromium(III) Complexes in Fluid Solution

N. A. P. KANE-MAGUIRE, C. G. TONEY and B. SWIGER,

Department of Chemistry, Furman University, Greenville, South Carolina 29613, U.S.A.

ARTHUR W. ADAMSON and R. E. WRIGHT

Department of Chemistry, University of Southern California, Los Angeles, California 90007, U.S.A.

Received February 2, 1977

Chromium(III) complexes display a rich photochemistry underligand field (LF) irradiation [1]; many exhibit room temperature solution phosphorescence [2]. Excitation energy transfer to chromium(III) complexes has also been established in room temperature fluid solutions, first with organic donors [2a, 3], and then with Ru(bipyridine)$_3^{2+}$ [4]. The efficiency of excitation energy transfer for a given donor, can vary considerably with the nature of the chromium(III) acceptor complex [3a, 5]. When the present study was initiated the only case in which *both* donor and acceptor species were chromium(III) complexes was that reported for *trans*-Cr(NH$_3$)$_2$(NCS)$_4^-$ (donor) and Cr(CN)$_6^{3-}$ (acceptor), at –65 °C [6]. The present investigation was undertaken to see if excitation energy transfer could occur between chromium(III) complexes in room temperature solution. We confirm and add to a recent report that such transfer can indeed occur [7].

The general process is that of Eq. 1. Species B is always Cr(CN)$_6^{3-}$ in this work,

$$^*A + B \underset{k_q'}{\overset{k_q}{\rightleftharpoons}} A + {}^*B \qquad (1)$$

and species A is one of the ammines of Table I. These complexes, especially B, are relatively weak and short-lived emitters in water solution and most measurements were therefore made in dimethylformamide (DMF) or dimethylsulfoxide (DMSO). Conditions were propitious for observing excitation energy transfer from a complex A to Cr(CN)$_6^{3-}$. The latter does not absorb in the wavelength region of the first LF band of any of the A species so that excitation could be restricted to A [1]. On the other hand, the emitting doublet states of the A complexes lie well above that of B in energy so that the forward process (1) should be favored. Figure 1 shows one sequence of emission spectra for 546 nm excitation of Cr(NH$_3$)$_5$(NCS)$^{2+}$ in DMF having various concentrations of B. The shorter wavelength emission is from the ammine, and decreases in intensity with increasing Cr(CN)$_6^{3-}$ concentration; at the same time, the longer wavelength emission from the cyano complex increases in intensity [8]. Clearly excitation energy transfer occurs. Analogous results were obtained in DMSO solution. In aqueous solution the intensity of *A emission again decreases with increasing Cr(CN)$_6^{3-}$ concentration. We could not establish, however, whether quenching was accompanied by excitation energy transfer since aqueous Cr(CN)$_6^{3-}$ does not detectably emit. Ion association was minimized throughout by making the solutions 0.5 *M* in neutral electrolyte, KCl in the case of aqueous systems, and [(C$_4$H$_9$)$_4$N](ClO$_4$) for the aprotic solvents, and appeared not to be important [9].

TABLE I. Emission and Excitation Energy Transfer Rate Constants at 25 °C.^{a}

Complex (Solvent)	Emission Lifetime^b τ^0 (μsec)	Bimolecular Rate Constants, M^{-1} μsec^{-1}			
		From Eq.(4)		From Stern–Volmer plots	
		k_q	k_q'	$k_{q,app}$	$k_{q,app}'$
Cr(en)$_3^{3+}$(H$_2$O)	1.3,^{c} 1.0				
(DMF)	0.95			613	
Cr(NH$_3$)$_5$(NCS)$^{2+}$ (DMF)	0.27, 1.1^d			894	
trans-Cr(en)$_2$(NCS)$_2^+$					
(H$_2$O)	2.05				
(DMF)	4.14	654	4.46	722	0.269
(DMSO)	3.16	282	2.52	270	0.274
cis-Cr(en)$_2$(NCS)$_2^+$					
(DMF)	0.24			660	
Cr(CN)$_6^{3-}$(H$_2$O)	–				
(DMF)	540^e, 491				
(DMSO)	116				

^{a} Data from this work unless otherwise indicated. Solutions were 0.01–0.04 *M* in A and 0.001–0.004 *M* in B. ^{b}For the ammines $\tau^0 = 1/k_{21}$ and for Cr(CN)$_6^{3-}$, $\tau^0 = 1/k_{34}$.
^{c}H. F. Wasgestian, R. Ballardine, G. Varani, L. Moggi and V. Balzani, *J. Phys. Chem.*, *77*, 2614 (1973) and ref. 2c.
^{d}3 °C. ^{e}See ref. 2c.

Measurements of lifetimes [11], τ, revealed an important complexity. Not only did τ_{*A} decrease with increasing B concentration, but also τ_{*B} *decreased with increasing A concentration.* Reverse excitation energy transfer (Eq. 1) evidently occurred. Plots of $1/\tau_{*A}$ *vs.* [B] were linear, as were those of $1/\tau_{*B}$ *vs.* [A], the slopes giving the Stern–Volmer rate constants $k_{q,app.}$ and $k_{q,app.}'$. Stern–Volmer kinetics are inadequate for our coupled reaction scheme, however. The scheme is:

$$(A, P) \xleftarrow{k_{21}} {}^*A \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} {}^*B \xrightarrow{k_{34}} (B, P') \qquad (2)$$

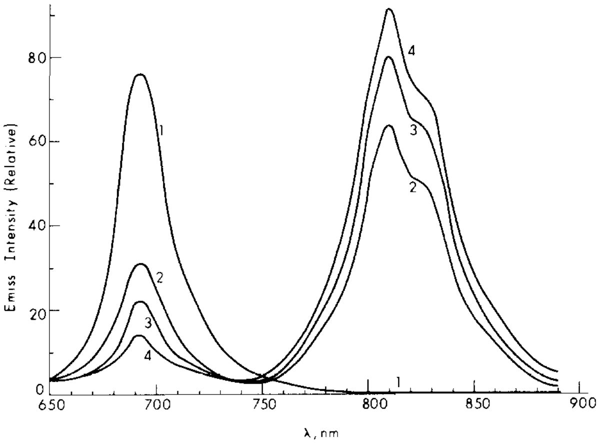

Fig. 1. Steady-state emission spectra on 546 nm excitation of 0.012 *M* Cr(NH$_3$)$_5$(NCS)$^{2+}$ in DMF containing the following concentrations of Cr(CN)$_6^{3-}$: (i) none, (2) 0.0038 *M*, (3) 0.0057 *M*, (4) 0.0114 *M*.

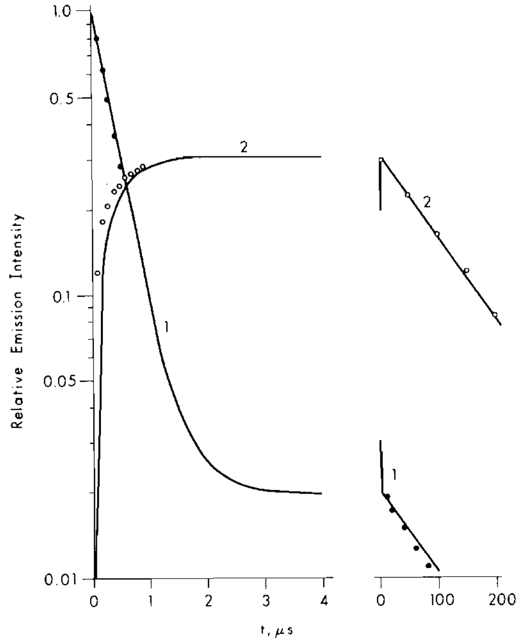

Fig. 2. Transient emission following 530 nm pulse excitation of a DMF solution 0.0105 *M* in *trans*-Cr(en)$_2$(NCS)$_2^+$ and 0.00306 *M* in Cr(CN)$_6^{3-}$. Curve 1: emission from *trans*-Cr(en)$_2$(NCS)$_2^+$ measured at 728 nm. Curve 2: emission from Cr(CN)$_6^{3-}$, measured at 810 nm. Solid lines: calculated curves; points: observed behavior as read from oscilloscope photographs.

where k_{23} and k_{32} are the pseudo first order rate constants k_q[B] and k'_q [A], respectively, k_{21} is the sum of all rate constants for the exciting of *A from the system (to A or to photoproducts P), and k_{34} is the sum for the exciting of *B (to B or to photoproducts P′). The general solution for coupled first order rate processes is well known [12]; that for equation (2) is:

$$
\begin{aligned}
{}^*A &= \frac{{}^*A_o}{\lambda_2-\lambda_1}\left[(\lambda_2-\alpha)e^{-\lambda_1 t}-(\lambda_1-\alpha)e^{-\lambda_2 t}\right] + \\
&\qquad \frac{{}^*B_o k_{32}}{\lambda_2-\lambda_1}\left(e^{-\lambda_1 t}-e^{-\lambda_2 t}\right) \\
{}^*B &= \frac{{}^*A_o k_{23}}{\lambda_2-\lambda_1}\left(e^{-\lambda_1 t}-e^{-\lambda_2 t}\right) + \\
&\qquad \frac{{}^*B_o}{\lambda_2-\lambda_1}\left[(\lambda_2-\beta)e^{-\lambda_1 t}-(\lambda_1-\beta)e^{-\lambda_2 t}\right]
\end{aligned}
\tag{3}
$$

where

$$2\lambda_{1,2} = (\alpha+\beta) \pm \left[(\alpha-\beta)^2 + 4k_{23}k_{32}\right]^{0,5} \tag{4}$$

and $\alpha = k_{21} + k_{23}$ and $\beta = k_{34} + k_{32}$. In our case, $^*B_o = 0$. Four quantities are known from each set of lifetime measurements: k_{21} and k_{34} from the lifetimes of *A and *B in the absence of bimolecular quenching, and λ_1 and λ_2, the decay times with both A and B present; k_{23} and k_{32} may then be found from equation (4), and hence k_q and k'_q. A set of observed and calculated decay plots is shown in Figure 2.

Because of the coupling of rate processes, k_q and k'_q are not the same as the apparent values from the Stern–Volmer slopes. For our systems, expansions correct in first order give

$$k_{q,app.}/k_q = 1 + k_{32}/k_{23};\; k'_{q,app.}/k'_q = (k_{21} - k_{32})/k_{23} \tag{5}$$

The correction is less than 10% in the case of $k_{q,app.}$, but $k'_{q,app.}/k'_q$ may be 0.1 or lower – see Table I. Thus where back excitation energy transfer occurs, *Stern–Volmer rate constants can be highly in error.*

Turning to the results, the k_q values in Table I are at about the expectation for rate limiting diffusional encounters; they also display the expected inverse dependence on solvent viscosity (η_{DMSO}/η_{DMF} = 2.5 at 25 °C), as do the k'_q values. The $k_{q,app.}$ values for the four ammine donors in DMF show little variation with charge or ligation. By contrast, with Ru(bipyridine)$_3^{2+}$ as donor, $k_{q,app.}$ varied by ten fold over a series of $Cr(en)_2XY^+$ acceptors [4c] and by a thousand fold if the series includes $Cr(CN)_6^{3-}$. The excited state of Ru(bipyridine)$_3^{2+}$ is charge transfer in character and likely is highly polarizable; this could explain the sensitivity of the quenching rate to the detailed nature of the acceptor. The behavior we observed may be the more normal one for excitation energy transfer between LF excited states.

Temperature studies are in progress to obtain an important quantity, the activation energy difference between k_q and k'_q. This difference gives a kinetic value for the energy difference between the doublet excited states of the Cr(III) complexes. Preliminary results place this value at about 10 kcal/mol for A = *trans*-Cr(en)$_2$(NCS)$_2^+$, or at about the spectroscopic value.

Acknowledgments

Support is acknowledged by N. K. M. for support from Research Corporation and the NSF–URP program, and by A. W. A., from NSF Grant No. CHE 74-08535 and ONR contract No. N00014-76-C 0548.

References and Notes

1 See E. Zinato in "Concepts of Inorganic Photochemistry" A. W. Adamson and P. F. Fleischauer, eds., Wiley, 1975.

2 (a) D J. Binet, E. L. Goldberg, and L. S. Forster, *J. Phys. Chem., 72,* 3017 (1968). (b) N. A. P. Kane-Maguire and C. H Langford, *Chem. Commn.,* 895 (1971). (c) H. F. Wasgestian, *J. Phys. Chem., 76,* 1947 (1972). (d) A. W. Adamson, C. Geosling, R. Pribush and R. Wright, *Inorg. Chim. Acta, 16,* L5 (1976).

3 (a) A. W. Adamson, J. E. Martin and F. Diomedi-Cammessei, *J. Am. Chem. Soc., 91,* 7530 (1969). (b) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Lawrence, *Coord. Chem. Rev., 15,* 321 (1975).

4 (a) J. N. Demas and A. W. Adamson, *J. Am. Chem. Soc., 93,* 1800 (1971). (b) I. Fujita and H. Kobayashi, *Ber. Bunsenges. Phys. Chem., 76,* 115 (1972). (c) F. Bolletta, M. Maestri, L. Moggi and V. Balzani, *J. Am. Chem. Soc., 95,* 7864 (1973).

5 (a) A. Adamczyk and F. Wilkinson, *J. Chem. Soc. Far. II 68,* 2031 (1972). (b) J. N. Demas and J. W. Addington, *J. Am. Chem. Soc., 96,* 3663 (1974). (c) H. F. Wasgestian and G. S. Hammond, *Theor. Chim. Acta, 20,* 186 (1971).

6 S. Chen and G. B. Porter, *J. Am. Chem. Soc., 92,* 3196 (1970)

7 F. Bolletta, M. Maestri and V. Balzani, *J. Phys. Chem., 80,* 2499 (1976).

8 The emission yields were obtained with the use of a modified Amino–Bowman spectrofluorimeter (Model 4-8203D) (see N. A. P. Kane-Maguire, J. E. Phifer and C. G. Toney, *Inorg. Chem., 15,* 593 (1976). One might suppose, in a sequence such as this, that a crossing point should be invariant. These emission spectra are for a kinetic situation, however, for which the sum of the concentrations of the emitting states, (*A + *B), is *not* a constant. No "isosbestic" behavior is expected, nor observed.

9 (a) The spectra of mixtures were essentially identical with those of the summed spectra of separate solutions, in either DMF or DMSO, and from 390 to 600 nm. (b) The Stern–Volmer quenching plot for Cr(NH$_3$)$_5$(NCS)$^{2+}$ showed some upward curvature, indicative of ion association [3b, 5b, 10]; the plot was linear, however, with the 0.5 *M* neutral electrolyte present. (c) With neutral electrolyte, the slopes of the intensity and lifetime Stern–Volmer quenching plots were essentially the same. Thus for aqueous Cr(en)$_3^{3+}$ at 22 °C the respective values were 550 and 582 M^{-1}.

10 F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J. Phys. Chem., 78,* 1374 (1974).

11 These were obtained by pulse excitation using 530 nm, 20 nsec pulses from the Q-switched, frequency doubled Nd laser system of ref. 2d. Solutions were changed frequently to avoid accumulation of photoproducts (from the ammine).

12 See S. W. Benson, "The Foundations of Chemical Kinetics", McGraw–Hill, 1960, p. 39.