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Energy Transfer between Hexacyanochromate and Reineckate Ions

Sir:

Although energy transfer from excited organic molecules to chromium(III) complexes has been studied,[1,2] there is some ambiguity about the state of the inorganic acceptor molecule reached. Schläfer, *et al.*,[3] have observed energy transfer from a series of Cr(III) double salts. However, there is evidence[4] that the observed effect is not caused by energy transfer but by a crystal perturbation. It is important to be able to populate and depopulate selectively at least one excited state of an inorganic complex in order to elucidate the pathways of the photophysical and photochemical primary processes. We describe here measurements of the energy transfer between the potassium salts of the reineckate ion (R), *trans*-$[Cr(NH_3)_2(NCS)_4]^-$, and the hexacyanochromate(III) ion (C), $[Cr(CN)_6]^{3-}$, by the quenching and sensitization, respectively, of the phosphorescence of the two complexes, and by lifetime measurements of the emission.

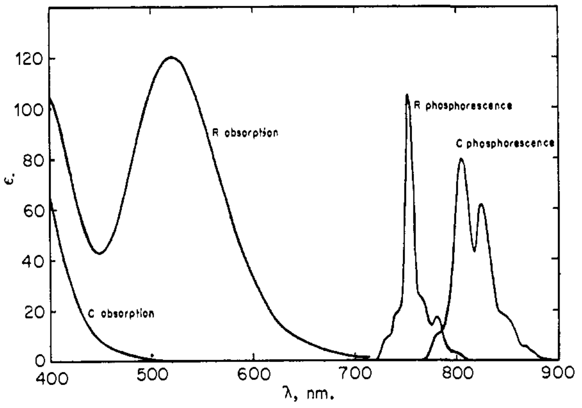

Figure 1. Absorption (25°) and phosphorescence (−65°) spectra of the donor, $[Cr(NH_3)_2(NCS)_4]^-$, and acceptor, $[Cr(CN)_6]^{3-}$, in methanol, water, and ethylene glycol (2:1:1) solvent.

The absorption spectra of R and C are sufficiently different (see Figure 1) that exciting light of wavelength 546 nm is absorbed only by R in solutions containing both ions. At 546 nm the $^4T_{2g}$ state[5] of R is populated directly, followed by intersystem crossing to the ^2E_g state which emits phosphorescence, $^2E_g \rightarrow {}^4A_{2g}$.[6] We find that in mixtures of the two ions phosphorescence of C also occurs and that the intensity of the phosphorescence of R is decreased correspondingly in the presence of C. The two phosphorescence spectra are easily separable, as shown in Figure 1. All measurements reported here were made with deoxygenated solutions[7] at −65° in the solvent methanol, water, and ethylene glycol in the ratio 2:1:1. Quenching and sensitization were studied at several concentrations of the acceptor, C, and at 0.05 *M* R with the results shown in Figures 2 and 3. For the donor (R) emission, Figure 2 shows a linear Stern–Volmer relationship between the ratio of the intensities of the unquenched to quenched emission and the concentration of C. The slope of the line, 24.3 M^{-1}, represents the product of the energy transfer rate constant (which includes possible quenching), k_{et}, and the lifetime of the phosphorescence decay of R, τ_R^0, in the absence of C. For the acceptor emission, the Stern–Volmer mechanism requires a plot of reciprocal intensity against reciprocal concentration of acceptor (Figure 3). In this case the Stern–Volmer constant, $k_{et}\tau_R^0$, is the ratio of the intercept of the line to its slope. The values so obtained at two peaks in the C phosphorescence spectrum, at 806 and 825 nm, are 20.7 and 21.8 M^{-1}, respectively.

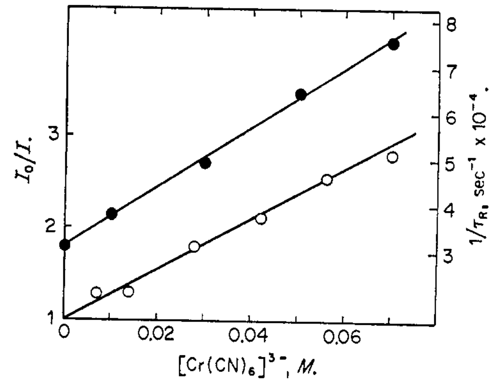

Figure 2. Stern–Volmer quenching of donor phosphorescence at −65° from steady-state intensity measurements (○) and from lifetimes (●) at 751 nm, [R] = 0.05 *M*.

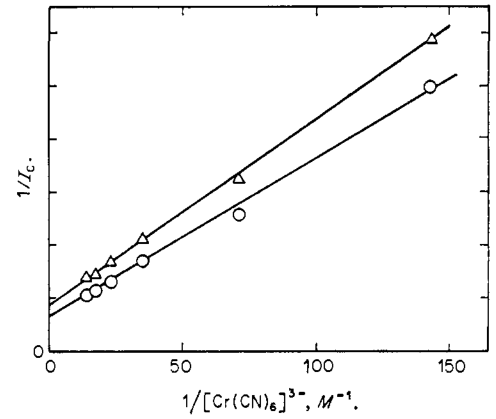

Figure 3. Sensitization of acceptor phosphorescence monitored at 806 nm (○) and at 825 nm (△), [R] = 0.05 *M* at −65°.

Lifetime measurements of the luminescence from solutions containing both ions were made using a flash

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(1) D. J. Binet, E. L. Goldberg, and L. S. Forster, *J. Phys. Chem.*, **72**, 2016 (1968).

(2) A. W. Adamson, J. E. Martin, and F. D. Camessei, *J. Amer. Chem. Soc.*, **91**, 7530 (1969).

(3) H. Gausmann and H. L. Schläfer, *J. Chem. Phys.*, **48**, 4056 (1968); H. L. Schläfer, H. Gausmann, and C. H. Mobius, *Inorg. Chem.*, **8**, 1137 (1969).

(4) A. D. Kirk and H. L. Schläfer, *J. Chem. Phys.*, **52**, 2411 (1970).

(5) We use the O_h symmetry designations for simplicity, although R is quadrate complex with D_{4h} microsymmetry.

(6) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964).

(7) Deoxygenation is necessary because oxygen quenches the emission at this temperature: A. Pfeil, submitted for publication.

lamp filtered to provide radiation near 500 nm so that again only R was excited. The phosphorescence decays of donor and acceptor could be measured separately by monitoring different wavelengths (Figure 1). They also have different decay lifetimes, 33 μsec for R and 380 μsec for C at −65°. From oscilloscope traces of the decay measured at 751 nm (at the phosphorescence maximum of R) a Stern–Volmer plot was obtained (Figure 2). The slope of this plot of reciprocal lifetime, $1/\tau_R$, against concentration of C gives directly the value of k_{et} as $6.6 \times 10^5\ M^{-1}\ sec^{-1}$. The emission at 840 nm (where only C emits) shows an initial increase in intensity with time followed by a longer decay. That increase represents the lifetime of the donor (R) excited state and the value obtained agrees with that found directly from the decay of R phosphorescence. The decay lifetime of C phosphorescence is somewhat smaller (250 μsec) in the presence of 0.05 M R than in its absence; thus, there is some back-energy-transfer from C to R or quenching by R. From these data, the reverse energy transfer rate constant, k_{et}', is calculated to be $2.7 \times 10^4\ sec^{-1}$. This is consistent with the fact that the reverse transfer must be endothermic by 870 cm^{-1}.

The lifetime of the phosphorescing state of R at −65° is 33 μsec in the absence of C. This value of $\tau_R{}^0$ can be used to find k_{et} from the steady-state Stern–Volmer constants. Using the average value of 22.3 M^{-1}, we find $6.9 \times 10^5\ M^{-1}$ for k_{et}, in good agreement with that found directly from lifetime measurements.

These results on quenching, sensitization, and lifetime establish unequivocally that the excited states of the donor and acceptor molecules involved are ^2E_g.[5] We cannot draw quantitative conclusions yet about the relative importance of energy transfer and of quenching reactions. It is apparent, however, that energy transfer from R to C is of major importance. With regard to the detailed mechanism, we also cannot distinguish the case that the phosphorescing state of R is directly involved in the transfer or that some thermally populated state is the immediate precursor to energy transfer. Our studies of the temperature dependence of k_{et}, to be reported in detail later, show that the lowest quartet state of R, about 16,000 cm^{-1} above the ground state, lies too high in energy to be involved in the transfer. Similarly, the $^4T_{2g}$ state of C cannot be involved. Energy transfer does not occur at temperatures below −130°, where the solvent becomes a rigid glass. This result, together with the magnitude of k_{et} itself, shows that energy transfer is a collisional process with a rate close to diffusion controlled ($k_{diff} \approx 4 \times 10^6\ M^{-1}\ sec^{-1}$ for our solvent estimated from viscosity measurements) at −65°. Energy transfer can not be detected at room temperature because the lifetime of the ^2E_g state of the donor decreases with increasing temperature faster than k_{et} increases and because of the importance of back-energy-transfer.

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An Unusual Complex Containing Bridging Vanadyl Groups. The Crystal Structure of N,N′-Propylenebis(salicylaldiminato)oxovanadium(IV)

Sir:

The yellow-orange color of the compound N,N′-propylenebis(salicylaldiminato)oxovanadium,[1] henceforth VO(salpn) with the formula $[OC_6H_4CH{=}NCH_2CH_2CH_2N{=}CHC_6H_4O]VO$, appears to be a striking deviation from most oxovanadium complexes which tend to be blue or blue-green.[2-5] Our preparative, structural, and spectroscopic studies of this compound have indeed revealed an unusual interaction in which the vanadyl oxygen acts as a ligand in the solid state and possibly in solution.

The compound can be prepared as reported[1] or in dimethyl sulfoxide or pyridine. In all cases sparingly soluble, yellow-orange needles are formed. The crystals are orthorhombic with cell dimensions of a = 7.538 (2), b = 11.874 (4), and c = 17.235 (5) Å. The space group is $P2_12_12_1$ and, with four molecules per unit cell, the calculated density is 1.495 g/cm^3 compared with the value 1.474 g/cm^3 measured by flotation.[6] Three-dimensional intensity data were measured using the stationary crystal–stationary counter method with Cu Kα radiation and an automatic diffractometer. All the hkl reflections with $2\theta \leq 135°$ were measured followed by a measurement of the hkl and $hk\bar{l}$ reflections within these limits, giving up to three measurements of an individual reflection. Averaging of equivalent reflections[7] led to 833 reflections that were considered to be observed and used in the analysis.

The structure was solved by locating the V–V vectors in the Patterson function and the light atoms in successive Fourier syntheses. The structure was refined by least-squares methods using isotropic and then anisotropic thermal parameters for all atoms. The final R index was 0.067 for only the observed reflections.

The crystal consists of VO(salpn) molecules packed so that the vanadyl oxygen atom of one molecule occupies the sixth position about the V atom in a neighboring molecule. The result is an infinite chain of molecules about a twofold screw axis linked by ···V–O–V··· bonds. The geometry and atomic numbering are shown in Figure 1. The V–O3′ (and V′–O3 in Figure 1) bond of 2.213 (9) Å which links the molecules is only slightly shorter than the V–O (water molecule *trans* to the vanadyl oxygen) distance of 2.235 (5) Å found in $[OV(H_2O)_4SO_4]H_2O$[8] or slightly longer than the V–N distance of 2.184 (12) Å found for a pyridine

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(4) R. C. Petterson, *Acta Crystallogr., Sect. B*, **25**, 2527 (1969).

(5) N. D. Chasteen, R. L. Belford, and I. C. Paul, *Inorg. Chem.*, **8**, 408 (1969).

(6) The small amount of long, thin needles available made the measured density less accurate.

(7) The averaging of the equivalent reflections hkl and $hk\bar{l}$ might introduce a small error in some reflections because of the anomalous scattering of vanadium. However, since the average consists of two values of hkl and one of $hk\bar{l}$, the effect is minimized. An evaluation of the effect of anomalous scattering will be carried out shortly.

(8) C. J. Ballhausen, B. F. Djurinskij, and K. J. Watson, *J. Amer. Chem. Soc.*, **90**, 3878 (1968).