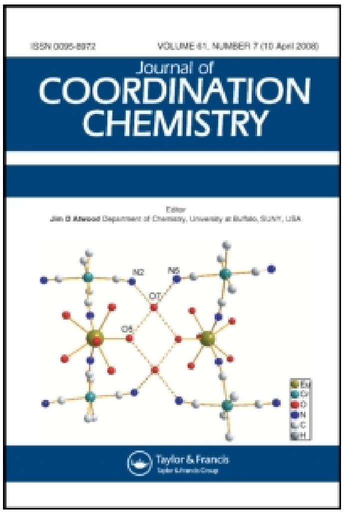

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PHOSPHORESCENCE IN MOLTEN TETRABUTYLAMMONIUM TRIBROMOMANGANATE

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The absorption and phosphorescence spectra and the phosphorescence lifetimes were measured for a series of fused salt solutions whose composition ranged between those of tetrabutylammonium tribromomanganate and *bis*-tetrabutylammonium tetrabromomanganate. The set of absorption spectra displayed an isosbestic point but the set of emission spectra was more complex. In mixed systems only a single lifetime was observed for the two different phosphorescence spectra indicating interconversion of the excited state species which were identified as four- and three-coordinate respectively. The graph of lifetime *versus* composition displays a pronounced curvature which is attributed to "structural quenching". A comprehensive kinetic scheme is proposed to represent the system.

INTRODUCTION

The properties of the phosphorescent molten salt system $(Bu_4N)_2MnBr_4$ were recently reported.[1] This system displays an absorption spectrum which is consonant with tetrahedral Mn(II). Dilution of this material with $(Bu_4N)Br$ produces little change in either the absorption or emission spectra. If, however, the phase diagram is followed in the direction of increasing mole fraction of $MnBr_2$ (towards the nominal composition $(Bu_4N)MnBr_3$) the intensity of the bright green luminescence falls off giving way to a deep red luminescence presumably signalling a significant change in the structure of the system. We report here the properties of this system and particularly the apparent interconversion of the emitting species. For brevity we will denote the solutions by their Br/Mn ratio; in this study it varies from 4:1 to 3:1.

EXPERIMENTAL

An interesting feature of the system is the fact that the solid 3:1 salt appears to be unstable with respect to the 4:1 salt and $(Bu_4N)Br$. Direct attempts to synthesize it failed and molten mixtures of the appropriate composition disproportionate on crystallizing. Consequently all experiments involving the 3:1 salt were performed on mixtures prepared, purified and handled in the molten state. Manganous bromide was synthesized from the metal since some batches of the commercially available salt were found to contain Co(II) producing internal absorption in the phosphorescence experiments. Recrystallized tetrabutyl-ammonium bromide was mixed with excess manganous bromide and melted under vacuum, filtered through UF sintered glass, frozen and stored in evacuated capsules. Attempts to dissolve enough manganous bromide in molten tetrabutylammonium bromide to lead to composition ratios less than 3:1 were unsuccessful. Furthermore, this compound, which phosphoresces red in the melt, cools to a red-phosphorescing glass. Upon standing (or abrupt quenching) it crystallizes with the development of a bright

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green phosphorescence. An examination revealed that the solid is composed of a mixture of crystals of manganous bromide and of *bis*-tetrabutylammonium tetrabromomanganate; *i.e.*, the 4:1 salt. In other words, the 3:1 salt appears to be a stable compound in the melt only. Like the 4:1 salt, it suffers very slow decomposition involving the organic ion in melts, but carefully purified samples may be kept in the range 120:140°C for several days without detectable changes.

An alternative procedure, useful for preparing intermediate compositions, was to prepare the 4:1 salt by a standard procedure,[1,2] mix it with the appropriate amount of tetrabutylammonium bromide, evacuate, melt and filter. All systems were analyzed before and after use by taking samples from the melt.

The absorption spectra were measured on a Cary Model 14 twin beam spectrophotometer which had been specially modified for high temperature operation and digitised for manipulation of the spectra. Emission was studied by front surface illumination of thermostated cells mounted in an Hitachi spectrofluorimeter, utilizing conjugate filters to reduce scattered light. After suitable baseline correction, this data was also digitised. Lifetimes were determined by the flash-decay technique; the time resolution of the instrumentation was 0.5 microseconds. Static magnetic susceptibilities were measured elsewhere[3] on a special automated Faraday balance and supplied to us. Conventional methods were used to measure the viscosity (hanging bob), viscosity (Ubbelohde viscometer) and epr spectra at the appropriate temperatures.

RESULTS AND DISCUSSION

The molar extinction coefficients for a set of compositions are shown in Fig. 1. There was little change with changing temperature so an intermediate temperature, 122.5°C, was chosen as an example. The absorbance between 18 kK and 24 kK increases slowly but steadily as the composition is changed from 4:1 to 3:1. The peaks at 26.5 and 27.7 kK in

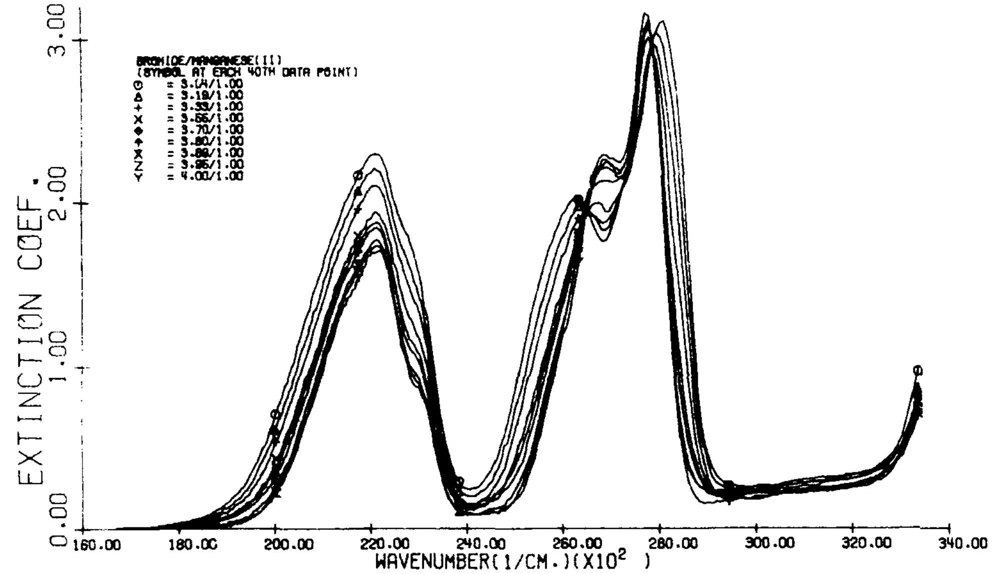

FIGURE 1 Molar extinction coefficients as functions of composition at 122.5°C.

the 4:1 salt separate as the composition moves towards 3:1 and are found at 26.1 and 28.0 in the 3:1 salt. No new peaks are seen as the salt composition goes from 4:1 to 3:1. The set displays isosbestic points which are generally considered to indicate the presence of several species in dynamic equilibrium. Linear combinations of the 3:1 and 4:1 salt spectra with the appropriate volume fractions as coefficients represent the observed spectra fairly well. The synthetic spectra and the difference between the synthetic and observed spectra are shown in Figures 2 and 3. The fit, while not perfect, is taken to be

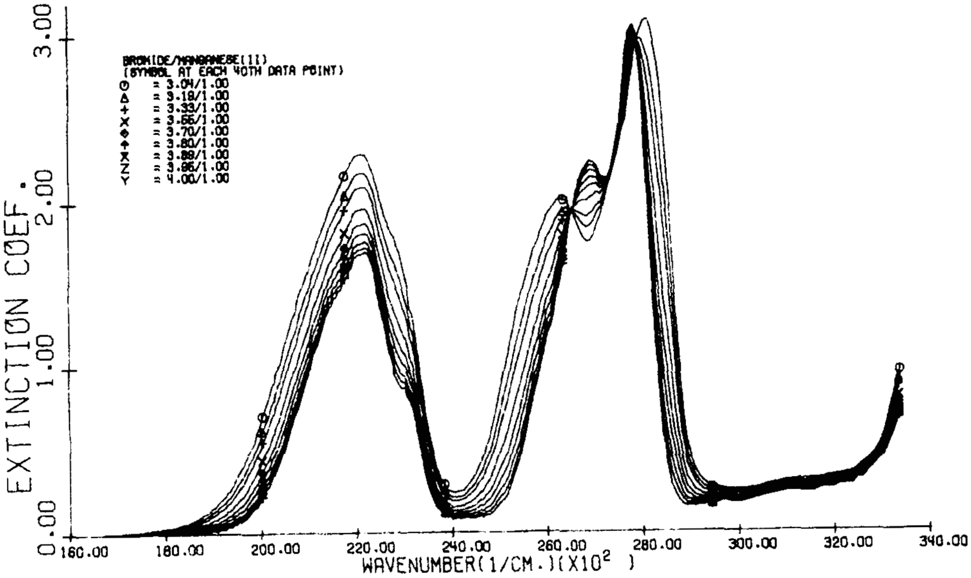

FIGURE 2 Molar extinction coefficients as functions of composition at 122.5°C estimated by taking linear combinations of the corresponding spectra of the 3:1 and the 4:1 compounds weighted according to the mole fractions.

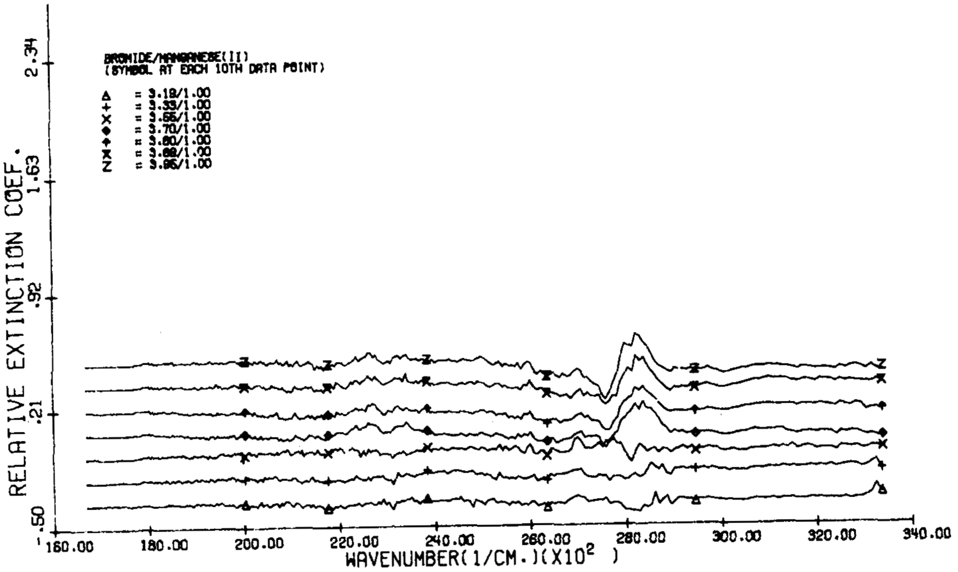

FIGURE 3 The differences between the spectra of Fig. 1 and Fig. 2 *i.e.*, the differences between the experimental and calculated spectra (note change of scale).

plausible evidence that the manganese ion occurs in these solutions essentially in only two kinds of environments. The small anomaly near 27.5-28.5 kK may result from the presence of a slightly different species or may be related to the tails of the strong charge transfer peaks in the ultraviolet region. Most probably, it indicates a modest failure in the linear combination model in that the local environment, *e.g.* the next nearest neighbors or the overall density have only a small influence.

The emission spectra, normalised to equal volume concentrations of manganese, are shown in Figure 4. The intensities fall off but the shapes of these curves do not change as the temperaure is increased (other temperature effects are discussed below in connection with lifetime measurements). The intensity of the green component decreases sharply as the composition varies from that of the 4:1 salt. The set does not display clearly defined isobestic points. If linear combinations of the emission spectra of the two pure molten salts are utilized to form synthetic spectra, the fit is very poor. Nevertheless, an important regularity is revealed when the differences between the synthetic and the observed spectra, which are shown in Figures 5 and 6, are examined; the set of differences roughly

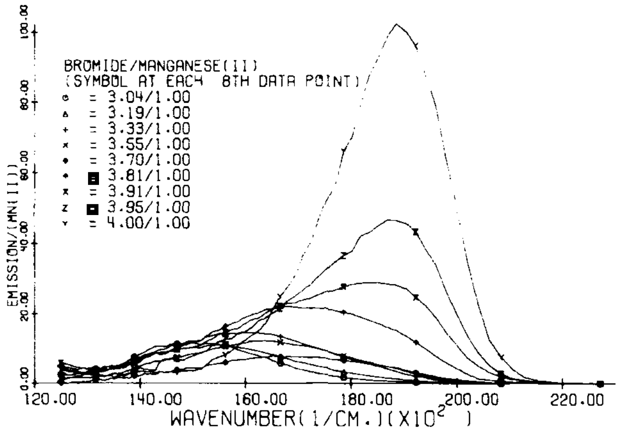

FIGURE 4 Emission spectra as functions of composition at 122.5°C. The relative intensities were adjusted by using equal intensities of the excitation source (385 microns) and dividing by the relative volume concentration of Mn(II). The relative emission spectra were not affected by shifting the excitation to shorter wavelengths.

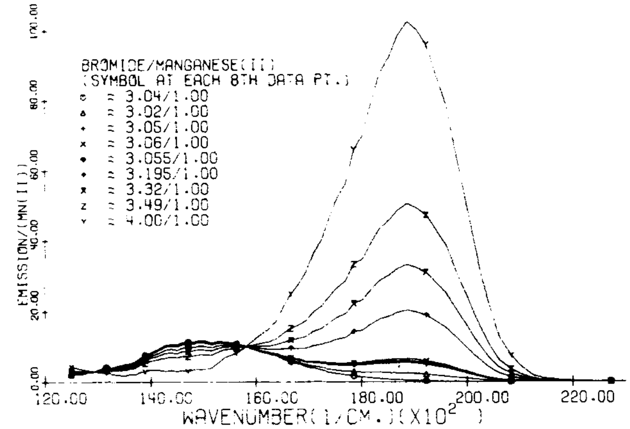

FIGURE 5 Emission spectra as functions of composition at 122.5°C estimated by taking linear combinations of the corresponding emission spectra of the pure 3:1 and 4:1 compounds with weighted according to the mole fractions.

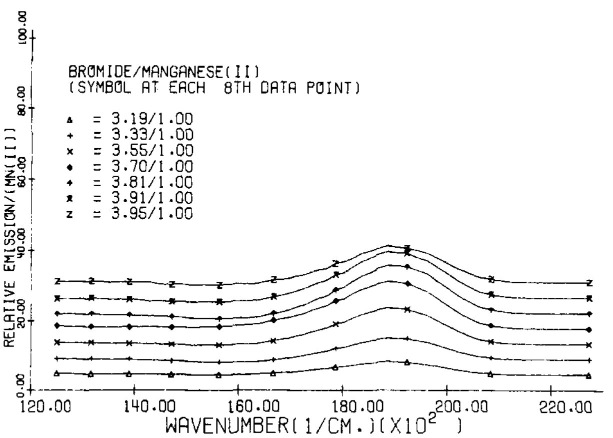

FIGURE 6 The differences between the spectra of Fig. 3 and of Fig. 3 *i.e.*, the differences between the experimental and calculated spectra (note the change of scale).

reproduces the shape of the pure 4:1 spectrum. This result strongly suggests that linear combinations of the pure spectra can represent the observed spectra but that the appropriate coefficients are not the stoichiometric ones. Thus the absolute intensity of the green spectrum appears to vary although its shape does not, presumably reflecting lifetime changes (see below). Accordingly, a new set of synthetic spectra was generated so as to obtain a best fit (least-squares criterion) with a free choice of coefficients. The results are summarised in Figures 7 and 8. On the whole, the results are compatible with the hypothesis that there are only two kinds of emitting sites but that their relative lifetimes change with composition.

There is an extensive literature concerning the spectrum of Mn(II) in various environments.[4–8] It is generally agreed that the lowest energy absorption of four-coordinate MN(II) arises from the $^4T_1$ state whereas the corresponding six-coordinate spectra involve the $^4E(^4T_1)$ levels. Pappalardo[5] found the lowest absorption peak for Mn(II) for octahedral sites in $MnBr_2$ at 18.45 kK; Vala *et al.*,[6] found the corresponding peak for tetrahedral Mn(II) in *bis*-tetrabutylammonium tetrabromomanganate at 21.14 kK. It is to be

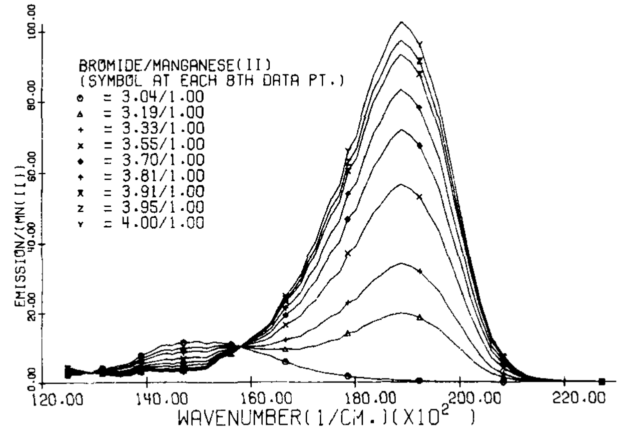

FIGURE 7 Emission spectra as functions of composition at 122.5°C estimated by taking linear combinations of the pure 3:1 and 4:1 compounds with weights chosen to optimize (in the least-squares sense) the fit to the experimental curves.

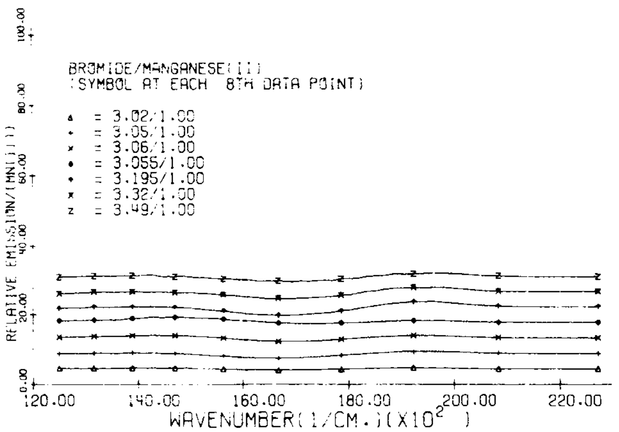

FIGURE 8 The differences between the spectra of Fig. 3 and of Fig. 5 *i.e.*, the differences between the experimental and calculated spectra (note the change of scale).

expected that spectra in molten salts will be somewhat "smeared" out by the increasing disorder, thermal population of higher vibronic states and collisional perturbations.[7]

The absorption spectra of the 3:1 and 4:1 molten salts are quite similar, showing small but distinct differences in the locations of the peaks. Both resemble the spectrum of crystalline tetrahedral tetrabromide salts[7] with a broad, lowest energy peak at 22.1 kK, that of the 3:1 salt having a tail extending a little further to long wavelengths. Their emission spectra, however, are quite different. Each is characterized by a broad featureless peak, but that of the 4:1 salt is shifted about 3 kK from its lowest absorption peak to 19.1 kK, whereas the Stokes shift of the 3:1 salt is to 15.0 kK, about 7 kK from its lowest absorption peak (which is nearly the same as that of the 4:1 salt).

The change in emission in passing from the 4:1 to the 3:1 compounds (although not the similarity in the absorption spectra) resembles the changes in the colour of the phosphorescence associated with changes in site symmetry for Mn(II) in other systems.[4,6,7] The green phosphorescence is always associated with tetrahedral site symmetry and the red one with octahedral structures.

The only geometries in which Mn(II) halides have been found to phosphoresce are tetrahedral and octahedral, so that one first thinks of identifying the red-phosphorescing 3:1 melt as containing octahedrally coordinated Mn(II). It is possible to reconcile the geometry with the stoichiometry by considering bridging structures wherein bromide ions could be shared between Mn(II) ions. The very large (Bu_4N) cations, however, separate the manganese halid groups by considerable distances, making bridging difficult. The chains or sheets that would result from such bridging would raise the viscosity considerably but there is little change in the observed viscosity (Table I) with composition. Furthermore, chains would imply end groups and chains of varying length in mixed systems, but the absorption and emission spectra indicate the presence of only two kinds of sites with no significant amount of intermediate structures.

Consequently, we were led to conclude that the red-emitting species in the 3:1 salt is, in fact, $MnBr_3^-$. This ion as such is unknown elsewhere but its occurrence here is reasonable for several reasons. The splitting of the 2.4 and 2.9 kK peaks in Fig. 1 as the composition changes from that of the 4:1 to that of the 3:1 salt can be interpreted in terms of changes from tetrahedral to trigonal coordination.[8] These two peaks are composed of three energy levels, namely, $^4T_2(D)$, $^4E(D)$, and $^4T_1(P)$ which are in order of increasing energy, the last two overlapping. The E estate is not split by a trigonal field but

TABLE I
Selected Physical Properties of the Salts.[a]

	4:1	3:1
Density (g cm^{-3})	1.455 – .00654T (C)	1.312 – .000730T (C)
Molar Volume (cm^3)	703.1	402.1
Viscosity (cp)	1538 – 10.71T (C)	1155 – 7.52T (C)
ESR spectrum	single broad line	single broad line
Magnetic Susc.	4.41 cm^3 T/mol	2.77 cm^3 T/mol
Magnetic Moment	5.93 Bohr magnetons	4.70 Bohr magnetons

[a] In mixtures, both the density and the viscosity were reasonablv well fitted by composition-weighted linear combinations of the values for the pure salts.

the T levels are split into A and E levels, which could produce the peak separation actually observed.

Changes in the position of the emission maximum with composition in glasses and and phosphors have been related[9] to a loosely defined term, "the space available to the Mn(II) ion". Lenver and Lehmann[10] observed that Mn(II) in non-cubic environments emits at lower energies than in cubic ones. In systems of lower symmetries, the single emission peak separates into two or more. They attributed this to splitting of the $^4T_1(G)$ and $^4T_2(G)$ states. Zink *et al.*,[7] in an examination of the triboluminescence of linear chain Mn(II) chloride compounds at 70 K, observed luminescence attributable to both the four- and six-coordinate sites simultaneously and noted that the peak locations moved to lower energies at higher pressures. The six-coordinate red-emitting sites in these chain compounds are of C_{3v} symmetry. After this work was done, an EXAFS study[11] demonstrated that the manganese in these 4:1 and 3:1 salts is indeed respectively 4-coordinated and 3-coordinated by bromide ions in these melts and is not bridged.

Since the absorption and emission spectra of systems of intermediate concentration (Figs. 1 and 4) indicate the presence of only two principal species, the question arises as to the rapidity of the exchange between Mn(II) in the different sites. Optical absorption spectra generally give no indication of the exchange time unless it is long compared with the time of the experiment (scarcely the case here). If the two species emitted quite independently, it would be expected that the lifetimes of the two emitting species as determined from the corresponding decay times at the separate peak wavelengths would differ. Chemical exchange, however, could result in collapsing together of the lifetimes so that only a single lifetime would be seen if the exchange process was fast compared with the shorter of the two lifetimes. The data in Table II support this latter model, indicating that the exchange between sites is short compared with the shortest time observed of 20 microseconds.

In order to understand the way in which the observed lifetimes vary with composition, we model the system by specifying a kinetic scheme. We imagine that a Mn(II) ion may find itself in either a T (3-coordinate) or F (4-coordinate) site, since only the two kinds of emission spectra are observed. Excitation, radiative and radiationless returns to the ground state and site exchange may take place. That is, the coordination sphere of the species may change upon excitation. Since only two kinds of emission spectra are observed, only two different kinds of sites are postulated. It is the continual rearrangements in liquid structures which are presumed to be responsible for the changes in local symmetry of the Mn(II) species. The set of reactions is as follows.

TABLE II
Phosphorescence Lifetimes.[a]

Br/Mn	Temperature (°C)			
	124.4	128.8	133.2	137.6
3.00	57.6	48.1	41.1	36.7
3.19	48.3	42.1	34.3	29.8
3.33	56.9	49.9	44.5	39.6
3.55	46.6	42.8	39.6	35.9
3.70	42.9	35.7	33.5	27.9
3.80	31.0	24.0	21.7	18.7
3.90	59.6	53.1	48.1	42.7
3.95	107.5	91.8	84.0	68.0
4.00	221.1	192.2	170.3	148.2

[a] Measured in microseconds. In each case, the lifetime appeared to be independent of the observing frequency. The reproducibility was of the order of several microseconds. There was no indication of systematic deviation from exponential decay.

1	$F + I_1(w_1) \rightarrow F^*$	k_1	(light absorption)
2	$F^* \rightarrow F + P(w_1)$	k_2	(phosphorescence)
3	$F^* \rightarrow F$	k_3	(quenching)
4	$T + I(w_2) \rightarrow T^*$	k_4	(light absorption)
5	$T^* \rightarrow T + P(w_1{}^*)$	k_5	(phosphorescence)
6	$T^* \rightarrow T$	k_6	(quenching)
7	$F^* + T \rightarrow = F + T^*$	k_7	(site exchange)
8	$T^* + F \rightarrow T + F^*$	k_8	(site exchange)

An important difference between site exchange and other excited state reactions is that here there must be conservation of sites in the sense that the total number of sites of each kind (excited plus ground state) is constant (thus the form of *7* and *8*). It is possible that there is a preference for the excitation to locate on one type of site, ordinarily that of lowest energy, but in the site exchange case the preference will be small, if it exists at all, because the small changes in packing and/or polarisation upon excitation must compete for effect with the much larger lattice energies. Consequently we expect that k_7 and k_8 will be similar or identical. The rate equations corresponding to this scheme are as follows.

$$d[F^*]/dt = -k_a[F^*] + k_b[T^*] + k_e$$
$$d[T^*]/dt = +k_c[F^*] - k_d[T^*] + k_f$$

where

$$k_a = k_2 + k_3 + k_3\,[T]$$
$$k_b = k_8[F]$$
$$k_c = k_7[T]$$
$$k_d = k_5 + k_6 + k_8[F]$$
$$k_e = k_1[F]\,I(w_1)$$
$$k_f = k_2[T]\,I(w_2)$$

For any given composition, [T] and [F] are effectively constant and proportional, respectively, to X and (1–X) where X is the fraction of the sites which are of T type. In the simplest model, these are in turn proportional to the mole fraction of the 3:1 and 4:1 salts although weighting factors may be required (see below). The observed emission will be given by $k_2[F^*]$ and $k_5[T^*]$. The well-known general solution to this pair of equations is shown below.

$$[F^*] = A\exp(mt) + B\exp(nt) + E$$

$$[T^*] = C\exp(mt) + D\exp(nt)$$

$$m = (1/2)(-k_a - k_d + R)$$

$$n = (1/2)(-k_a - k_d - R)$$

$$R^2 = (k_a - k_d)^2 + 2k_bk_c$$

The coefficients A-E are determined by the boundary conditions. For example, if we imagine the excited state of F, namely F*, to be initially populated by a short intense pulse of light at w and that the excited state of T, namely T*, is simultaneously populated with a short intense pulse of light at w_2, the coefficients are given by the following expressions.

$$A = (m + k_a)([F^*] - k_b[T^*]_o)/(m-n)$$

$$B = [F]_o - A$$

$$C = k_c[F]_o - (k_d + m)[T^*]_o/(m-n)$$

$$D = [T^*]_o - C$$

$$E = F = 0$$

If the exchange steps *7* and *8* are very slow compared with the other steps, the exponents m and n are approximately k_a and k_b respectively. That is, each of the species

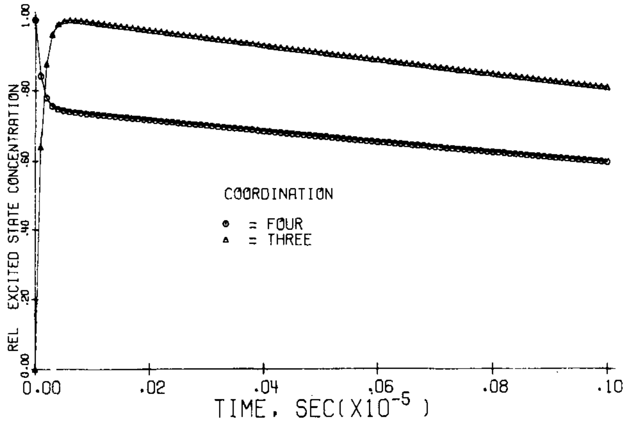

FIGURE 9 Representative intensity/time curves calculated from the kinetic model) (equations *1-8*). The parameters were chosen to illustrate the properties of the model.

displays a decay which is the sum of two exponentials. Since only one exponential and hence one lifetime was observed in the experiments reported here, this limiting case is not applicable. The other extreme occurs when the exchange steps *7* and *8* are rapid compared with the other steps. For convenience we take $k_7 = k_8$ and $[\bar{T}] + [F] = 1$. Then the coefficients m and n may be approximated as follows, $m = k_7$ and $n = X(k_2 + k_3) + (1-X)(k_5 + k_6)$ leading to expressions for the concentrations which, after a brief transition region of lifetime approximately 1/m, decay with a lifetime 1/n (see Figure 9). This model successfully predicts a single lifetime in the intermediate composition region.

The general shape of the lifetime composition curve (Fig. 11, upper curve) is reproduced except that the experimental curve (Fig. 10) displays a much more pronounced curvature. A simple and plausible extension of the model to account for this phenomenon as well can be provided by the postulate that there is an enhanced rate of quenching in the mixed systems related in some way to the loss of local site symmetry. A slightly different postulate which leads to the same result is that the excited species becomes more vulnerable to quenching in the actual process of site transformation. In either case, the

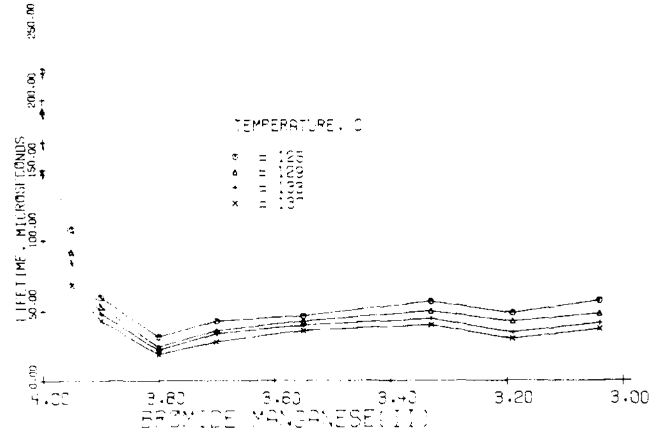

FIGURE 10 Experimental lifetime/composition curve.

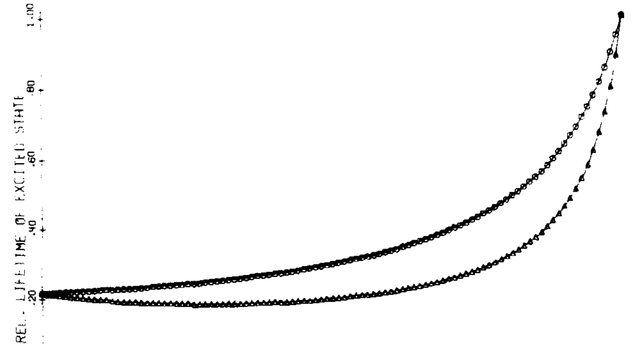

FIGURE 11 Representative lifetime/composition curves calculated from the extended kinetic model (equations *1-10*). The parameter k, was given two different values (zero for the upper curve) in order to illustrate its effect in producing a dip in the curve so as to improve the agreement with Fig. 10.

probability of such quenching may be expected, at the lowest level of approximation, to be proportional to an expression of the form $k_9X(1-X)$, since it must go to zero at the extremes of composition and reach a maximum in the intermediate range. The new steps are given by *9* and *10.*

9 $T^* \rightarrow T$ k_9 (structural quenching)
10 $F^* \rightarrow F$ k_9 (structural quenching)

These two steps may be thought to represent a quenching action due perhaps to the decrease in local symmetry that must occur in mixtures of intermediate composition. Alternatively they may be thought of as representing quenching that takes place during the change from one coordination geometry to the other and might be pictured as a transition state which is easily quenched. Incorporating these steps into the kinetic scheme modifies the expressions for k_a and k_d by adding to each a term of the form $k_9X(1-X)$.

The solution to the general problem for boundary conditions where only the F* species is initially populated is given so as to most clearly illustrate the relative roles of the transient and the longer term decays.

$$[F^*] = ([F^*]_o/Rt)\,(n-k_d)\exp(-nt) - (m-k)\exp(-mt)$$

$$[T!^*] = ([F^*]_o/Rt)\,(\exp(-nt) - \exp)-mt))$$

Useful limiting forms are awkward to express. Numerical evaluations of the concentration/time curves and of the apparent lifetimes for two different values of the structural quenching constant are shown in Fig. 11. The role of the structual quenching constant in depressing the middle of the lifetime/composition curve is made evident. The observed lifetime/composition curve can be seen to be satisfactorily modelled *in toto* by this extended kinetic scheme.

Finally we may comment on site symmetry in what is, after all, a liquid system. In a fused salt,[12] the packing energies of the ions far exceed ligand field energies, so that the chemical nature of the Mn(II) ion is unimportant except for its charge and size. Structures may be expected to occur in liquids which are quite different from those found in crystals because of the removal of the condition for precise periodicity. The molecular dynamics calculations of Sundheim and Woodcock[13] dealt with a model of a mixture of mono- and di-valent cationic halides corresponding roughly to the system K_2MgCl_4. The striking observation they made was that the pair distribution function for the halide about the Mg(II) ion peaked sharply and had an area corresponding to 4 nearest neighbors, shifting to 3 in response to relatively small changes in ionic radius. This result suggests that the structure of transition metal halide complex ionic melts may also be determined principally by packing and that the ligand field spectrum is determined in turn by symmetry and field strengths so imposed. Thus, the non-directional coulombic and hard-sphere forces enforce a more or less well-defined geometry about the Mn(II) ion to a much larger extent than has been generally recognized.

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