Intersystem Crossing and Internal Conversion from the Lowest Charge-transfer Singlet Excited State of the (2,9-Dimethyl-1,10-phenanthroline)copper(I) Cation

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Summary Sensitized *P*-type delayed fluorescence is employed to determine the energy of the lowest charge-transfer triplet state and the singlet–triplet intersystem crossing yield in (2,9-dimethyl-1,10-phenanthroline)-copper(I); internal conversion to the ground state is the dominant decay mode of the lowest excited singlet state of this chelate.

While the significance of nonradiative intersystem crossing from 'spin-allowed' to 'spin-forbidden' intramolecular charge-transfer (c.t.) excited states of co-ordination compounds has been implied by photoluminescence[1] and photochemical[2] studies, determination of intersystem-crossing efficiencies and energies of 'spin-forbidden' c.t. states in metal complexes has received virtually no attention. We previously described the redox photochemistry of copper(II) complexes with 2,9-dimethyl-1,10-phenanthroline (dmp),[3] and noted that the corresponding copper(I) species were nonluminescent and photochemically inert despite the presence of a low-lying singlet → singlet metal → ligand c.t. transition in their electronic spectra.[4] We now report a study of energy-dissipation processes in the lowest c.t. singlet of $Cu(dmp)^+$ in ethanol.

The intersystem-crossing yield (ϕ_{ISC}) of a compound can be determined by measuring the intensity and lifetime of sensitized delayed fluorescence (d.f.) of suitable triplet acceptors.[5] The measurement is comparative—*i.e.*, the triplet yield of the compound of interest is measured relative to that of a 'standard' of known ϕ_{ISC}. We have used anthracene ($\phi_{ISC} = 0{\cdot}70^5$) and naphthacene ($\phi_{ISC} =$

0·63[6]) as 'standards' with the triplet acceptors listed in the Table.

TABLE

Acceptor	E_T (kJ mol^{-1})[7,8]	Sensitized d.f.?	ϕ_{ISC}[a]
Pyrene	201·5	No	—
Anthracene	177·7	No	—
3,4-Benzpyrene ..	175·1	Very weak	<0·01
9-Methylanthracene ..	169·7	Weak	0·05 ± 0·02
Perylene	150·5	Strong	0·27 ± 0·02
Chlorophyll b	138·6	Strong	0·26 ± 0·04
Chlorophyll a	120·1	Strong	0·24 ± 0·02

[a] Assuming unit transfer efficiency to acceptor.

Inasmuch as triplet-triplet energy transfer is normally inefficient when E_T for the donor and acceptor are nearly equal, the data indicate an energy of 165 ± 5 kJ mol^{-1} for the lowest c.t. triplet of Cu(dmp)$^+$. The energy of the lowest c.t. singlet of Cu(dmp)$^+$ is 183 kJ mol^{-1}. In view of the small singlet-triplet split, ϕ_{ISC} is surprisingly low [the excellent agreement of the values obtained from sensitized d.f. of perylene and chlorophylls a and b establish that $\phi_{ISC} = 0{\cdot}26 \pm 0{\cdot}04$ for Cu(dmp)$^+$ in ethanol]. It is therefore evident that internal conversion to the ground state is the major de-excitation mode of the lowest c.t. singlet of Cu(dmp)$^+$. These results provide strong evidence that internal conversion of 'spin-allowed' c.t. states to the ground state can be a dominant process in the photophysical behaviour of co-ordination compounds.

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