Photochemistry of Macromolecular Bound Cobalt(III) Ammine Complexes

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Quantum yields for the redox decomposition of *cis*-$[Co(en)_2(pvp)X]^{2+}$ [en = ethylenediamine; pvp = poly(vinylpyridine), X = Cl or Br] ions are significantly affected by the presence of the macromolecular ligand.

Photoirradiation of cobalt(III) ammine complexes in the charge transfer from the ligand to the metal band results in the reduction of the metal centre by the ligand.[1] It has been observed that the excited state processes of cobalt(III) complexes leading to product formation are influenced by the solvent media.[2] In particular water molecules surrounding the excited states appear to play an important role in the formation of cobalt(II) ion from the excited state.[3,4] In order to investigate the redox properties of co-ordination compounds with macromolecular-ligands we have prepared co-ordination compounds with poly(vinylpyridine) and report the photochemical properties of the macromolecular complexes.

cis-$[Co(en)_2(pvp)X]^{2+}$ *cis*-$[Co(en)_2(py)X]^{2+}$
(**1**), X = Cl (**3**), X = Cl
(**2**), X = Br (**4**), X = Br

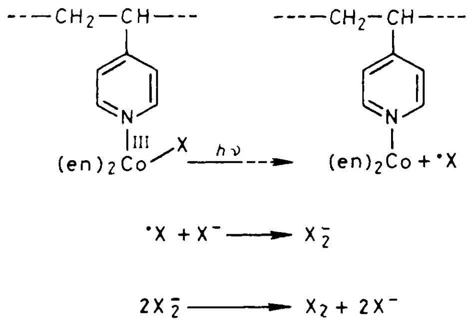
py = pyridine, pvp = poly(vinylpyridine)

Poly(vinylpyridine) condensed with *trans*-$[Co(en)_2X_2]^+$ (en = ethylenediamine) (X = Cl or Br), to produce the macromolecular complexes (**1**) and (**2**). Complexes (**3**) and (**4**) were synthesized as described in the literature.[5] Aqueous solutions of the polymeric and monomeric complexes in 0.1 M $HClO_4$ were irradiated at 315 nm using a 300 W EIMAC xenon lamp. Cobalt(II) ion produced during the photolysis was estimated[6] and the quantum yields for cobalt(II) formation are summarized in Table 1; for the complexes with polymeric ligands the number of cobalt centres co-ordinated to the polymer for a given number of pyridine sites in the macromolecular chain was varied and the quantum yields for cobalt(II) were determined. Flash photolysis of the monomeric and polymeric complexes showed transients and their absorption spectra exhibited maxima around 340 nm for (**1**) and (**3**) and at 360 nm for (**2**) and (**4**) in excess of Cl^- and Br^- respectively. Flash photolysis of both monomeric and polymeric complexes yielded transients with λ_{max} 340 nm [due to Cl_2^-, from (**1**) and (**3**)] and 360 nm [due to Br_2^-, from (**2**) and (**4**)] indicating charge-transfer (C.T.) breakdown on exciting in the Co^{III} X^- C.T. band (Scheme 1).

Table 1. Quantum yield for cobalt(II) formation from monomeric and polymer cobalt(III) complexes, excitation wavelength 315 nm.

Complex	% of complex[b]	$\Phi(Co^{2+})$[a]
(**3**)	—	0.0124
	42.30[c]	0.0130
(**1**)	9.95	<0.003
	12.20	<0.003
	16.44	0.0078
	37.44	0.0093
(**4**)	—	0.062
	30.00[c]	0.067
(**2**)	2.65	0.0160
	4.00	0.0210
	5.60	0.0224
	6.70	0.0230
	19.20	0.0252

[a] Average from three experiments: deviation ±10%. [b] % of pyridine units in pvp bound to cobalt(III) complex: determined by reducing the bound cobalt(III) and estimating the cobalt(II) in a given sample of the polymeric complex. [c] Concentration of pvp added: expressed as $100\,c/(c + p)$ where c is the concentration of the cobalt(III) monomeric complex and p the moles of pyridine units in the pvp.



Scheme 1

It is well known[1] that cobalt(III) ammine complexes on irradiation in the charge transfer-to-metal band undergo redox decomposition. What is of particular interest is that with the change in the number of cobalt(III) centres present in a macromolecular chain the quantum yield for cobalt(II) is affected. The absorption spectra of the monomeric complexes and the polymeric complexes are almost identical above 250 nm and the excited states produced on optical absorption should have very similar electronic structure. For the monomeric complexes there is no concentration effect on the quantum yield and, as seen from Table 1, addition of macromolecular ligand to the solvent medium does not affect the cobalt(II) quantum yield.[8] Thus the quantum yield variation for cobalt(II) observed for the macromolecular complexes as a function of the extent of metal co-ordinated to the polymer should be attributed to the polymeric environment around the photoreactive excited state. At 315 nm only the cobalt(III) complex absorbs and poly(vinylpyridine) has negligible absorption.

The macromolecule poly(vinylpyridine) is known[9] to be present in solution in a coiled structural form and the number of solvent water molecules present around the cobalt(III) complex depends on whether the cobalt(III) centre is buried inside the polymer coil or is at the outer edge of the coil where more water molecules are present around the complex ion.[10] With more cobalt(III) centres bound to the macromolecular chain the macromolecule would assume a more linear chain structure since the greater number of dipositive cobalt(III) complexes present in the chain would tend to repel each other. As a consequence more water molecules would be present around the linear chain than around the coiled macromolecules. Thus the decreasing cobalt(II) quantum yield with decrease in the extent of condensation of the metal complex to the macromolecule indicates that water molecules around the excited species of the cobalt(III) complex induce the formation of cobalt(II) ion from the excited state.

The charge-transfer excited states of cobalt(III) complexes do not emit, the lifetimes are probably less than 10^{-9} s, and the redox reaction probably occurs as fast as solvent relaxation itself around the excited state. Involvement of water molecule in the formation of cobalt(II) ion occurs within this time domain. There are not many reports[7] on the photochemistry of co-ordination compounds with macromolecular ligands and from this study it appears that redox reactions in macromolecular media similar to biological systems are influenced by the environment.

We thank the Department of Science and Technology and U. G. C. for financial assistance.

Received, 22nd December 1982; Com. 1469

References

1 V. Balzani and V. Carassiti, 'Photochemistry of Coordination Compounds,' Academic Press, New York, 1970.
2 'Concepts in Inorganic Photochemistry,' eds. A. W. Adamson and P. D. Fleisauer, Wiley, New York, 1975.
3 P. Natarajan, *J. Chem. Soc., Dalton Trans.*, 1977, 1400.
4 P. Natarajan and A. Radhakrishnan, *J. Chem. Soc., Dalton Trans.*, 1982, 2403.
5 Y. Kurimura, E. Tsuchida, and M. Kaneko, *J. Polym. Sci., Sect. A*1, 1971, **9**, 3512.
6 R. E. Kitson, *Anal. Chem.*, 1959, **22**, 664.
7 M. Kaneko, S. Nemoto, A. Yamada, and Y. Kurimura, *Inorg. Chim. Acta*, 1980, **44**, L 289.
8 P. Natarajan, *J. Chem. Soc., Chem. Commun.*, 1975, 526.
9 P. J. Flory, 'Principles of Polymer Chemistry,' Cornell University Press, Ithaca, New York, 1953.
10 D. O. Jordan, A. R. Mathieson, and M. R. Porter, *J. Polym. Sci.*, 1956, **21**, 473.