

Stabilisation of Cobalt(I) by Coordination within a Bipyridyl-based Hydrogel Polymer Membrane

A. L. Lewis and J. D. Miller*

The Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET, UK

A method is described for the preparation of a polymer-bound tris(2,2'-bipyridine)cobalt(I) complex; within the dehydrated hydrogel membrane this oxidation state is unusually stable and easy to handle in air.

Cobalt(I) complexes have been of interest for a considerable time, and with 2,2'-bipyridine (bpy) as ligand, this oxygen-sensitive oxidation state has been known since 1957.¹ The tris(bpy)cobalt(I) complex is a powerful reducing agent, with reported E^0 values ranging from 1.0 to 1.37 V (vs. standard calomel electrode, SCE).² It has therefore found use in a variety of catalytic applications, including the photoreduction of water.³ Here we report a variation that permits this grouping to be readily prepared, handled and stored in the open laboratory.

Our approach uses copolymeric hydrogels, which already find use as biomaterials,⁴ as ion-exchange materials⁵ and in the immobilisation of catalytically active complexes.⁶ Hydrogels rapidly attain high equilibrium water contents (EWCs) into which salts can diffuse. The water also plasticises the highly mobile polymer chain segments, producing materials that can be classed as homogeneous.⁷ Hydrophobic copolymers containing derivatives of bipyridine are well known,⁸⁻¹¹ but hydrophilic copolymers have been reported only infrequently.¹²

Table 1 Preparative, spectroscopic and redox data for Co-coordinated bipyridine based hydrogel membranes and monomeric complex analogues

Ligand loading (by wt.)	EWC (%)	HEMA : vbpy mole ratio	Complex type	λ_{\max}/nm	Cycle	% Co lost after each redox cycle	
						Ligand loading	
						0.5%	8%
0	41.1	—	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	515 ^a	1	16.6	6.5
0.05	39.7	3010 : 1	$[\text{Co}(\text{bpy})_3]^{2+}$	455 ^a	2	12.4	4.9
0.1	38.9	1500 : 1	$[\text{Co}(\text{bpy})_3]^+$	600 ^b	3	6.5	2.7
0.25	39.2	601 : 1	$[\text{Co}(\text{vbpy})_3]^{2+}$	455	4	3.3	1.6
0.5	39.1	300 : 1	$[\text{Co}(\text{vbpy})_3]^+$	600	5	3.0	1.3
1	38.2	149 : 1	$[\text{Co}(\text{Pbpy})_3]^{2+}$	455 ^c	6	2.8	0.7
2	38.1	74 : 1	$[\text{Co}(\text{Pbpy})_3]^+$	600 ^c			
4	37.9	36 : 1					

^a Ref. 15. ^b Ref. 17. ^c vbpy refers to the free ligand and Pbpy to the polymer-bound species.

We have studied complexation of metal ions to membranes fabricated from copolymers of 2-hydroxyethyl methacrylate (HEMA), and 4-methyl-4'-vinyl-2,2'-bipyridine (vbpy). The consideration of reactivity ratios suggest^c that the pendant bipyridine groups will be randomly distributed within the copolymer chains. The membrane form is used to ensure reproducibility of manufacture and to allow direct comparison with other systems.^{13,14} Bubble-free membranes of 0.4 mm thickness were prepared by an established method,¹⁵ from a mixture of monomers, which also contains 0.5% by weight of azoisobutyronitrile as a free radical initiator and 1% by weight of ethyleneglycol dimethacrylate as a cross-linking agent. After fabrication the membranes are left to hydrate in distilled water for at least one week, with frequent changes of water. We have copolymerised a range of monomer mixtures (Table 1), throughout which the resulting membranes remain homogeneous.

The coordinative capacity of pre-hydrated membranes was assessed by immersing samples in 0.25 mol dm⁻³ CoCl₂ solutions for a number of days. The surfaces of the membranes were then swiftly rinsed and dried before the metal content was determined by acid digestion of the organic matter, followed by analytical atomic spectrometry (AAS) studies on the residual metal oxide. This measures both the cobalt bonded to the polymer and that present in the imbibed water. Thorough leaching of the solvated ions from the membrane prior to digestion leads to a Co : vbpy ratio of approximately 1 : 3, and provides the expected variations in the visible absorption maxima consistent with a change in coordination from $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ to $[\text{Co}(\text{vbpy})_3]^{2+}$ (Table 1).¹⁶ Alternatively, the monomeric $[\text{Co}(\text{vbpy})_3]^{2+}$ complex can be synthesised directly,¹⁷ and then copolymerised with HEMA. The membranes prepared by the two methods are indistinguishable.

When the membranes containing polymer-bound $[\text{Co}(\text{vbpy})_3]^{2+}$, made by either method, are immersed in an aqueous solution of excess of NaBH₄, dihydrogen is evolved and the membranes take on an intense blue colour. Visible spectra are identical to those seen for the free Co^I complex in solution (Table 1).¹⁸ A strong band at 600 nm and a 430 nm shoulder on an intense, off-scale UV band can be easily monitored for the 1–4% vbpy-loaded range of membranes.

The monomeric Co^I complex is sensitive to reoxidation by O₂,¹ as also are our reduced, hydrated membranes. Thus, when a 2% loaded membrane containing $[\text{Co}(\text{vbpy})_3]^{2+}$ is reduced, rinsed and placed in 100 ml of unstirred distilled water at 25 °C contained in an open beaker, the blue colour is completely lost in a slow, first-order decay process ($t_{1/2} = 47$ min) as oxygen dissolved in the water permeates the membrane.

Samples of all our cobalt-containing membranes were subsequently subjected to a regime of six repetitive reduction–oxidation cycles, and the cobalt content was monitored spectrophotometrically at the end of each cycle. The data

presented in Table 1 show that much of the metal is lost within the first two cycles, and a greater proportion is lost from the membranes containing lower vbpy loadings. Subsequently, smaller and constant fractions of the residual metal are lost each time. After six cycles between 80 and 55% of the $[\text{Co}(\text{vbpy})_3]^{2+}$ still remains, a factor dependent on the original ligand-loading.

It is known that dehydration of polyHEMA renders it impermeable to oxygen because the gas transport medium has been removed.¹⁹ That also occurs here. If, immediately after reduction, Co-containing membranes are dehydrated in an oven at 60 °C and then exposed to the atmosphere, the blue colour remains for days rather than hours. Under ambient conditions the rate of loss of intensity at 600 nm appears to be of zero order, with only a 30% reduction occurring in 100 hours. We attribute that slow loss to the initial uptake of atmospheric moisture, as a membrane kept under air but in a desiccator will retain its colour indefinitely. These prepared membranes provide an easily handled form in which to keep Co^I until it is required. The technique should also be applicable to other air-sensitive species.

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