Supplementary information:

Cobalt(III) complexes as functional *ligands* for metal (oxide) surfaces

Rachel J. Cooper[a], Reuben T. Jane[b], Thomas E. Jeffs[a], Richard M. Hartshorn*[b] and Peter A. Tasker*[a]

Experimental

All reagents and solvents were used as received from Sigma Aldrich, Fluka and Lancaster. The goethite substrate, Bayferrox® 415 was obtained from Bayer. Aluminium flake was supplied by Eckart (STAPA Metallux R8754 paste – 65 % Al by weight with 50 % of particles < 20 μm). Water was purified before use with a Milli-Q® water purification system.

Complexes 1-5 were synthesised as previously described,[1] and ICP-OES data were obtained using a Perkin Elmer Optima 5300 DV instrument with curve fitting performed using OriginLab©, and XPS data was recorded using a VG Scientific Sigma Probe.

To determine isotherms, aqueous stock solutions (*ca.* 5×10^{-3} mol dm^{-3}) of the cobalt(III) complexes shown in Fig. 2 were prepared. Accurately pre-weighed quantities of goethite, (*ca.* 0.4 g) in polycarbonate centrifuge tubes were stirred with a solution of the complex in water (10.0 cm^3) of known concentration for 2 hr at 25 °C. The mixtures were centrifuged, filtered under pressure (N$_2$) through glass microfibre paper, and the resulting supernatants were analysed for their elemental content (Co and Fe) by ICP-OES. The measured cobalt content remaining in solution allowed the amount adsorbed onto goethite to be calculated. The iron content was measured as a precaution to eliminate possible interferences; no significant levels (< 1 ppm) were detected in the aqueous phase after equilibration.

The data, plotted using Origin, were subjected to a non-linear curve fit. By default, the maximum surface coverage (*A*) and equilibrium adsorption constant (*K*) were obtained from the standard Langmuir adsorption isotherm where *y* is the surface coverage, *c* is the residual complex concentration in solution, and $c^{\theta} = 1$ mol dm^{-3}.

$$y = \frac{AK(c/c^{\theta})}{1+K(c/c^{\theta})}$$

Hydrogen evolution measurements were carried out using Avecia standard procedures[2] using the glassware shown in Figure S1. The round-bottomed flask containing the test mixture was immersed in a thermostated water bath (52 °C). The mixture was allowed to equilibrate for 1 h to allow surface complexation to occur. After 1 h the screw cap was closed. The volume of water displaced to the upper chamber was monitored regularly (the total volume available to be displaced was 80 ml). The aluminium flake sample, Eckart STAPA Metallux R8754 consists of 65 wt % of > 99.9 % pure aluminium and 35 % wt % of a hydrocarbon solvent. Synperonic NP8, a non-ionic surfactant, was added to improve the wetting of the hydrophobic aluminium flake. The passivating ligand (2 mmol) was added in substantial excess of the theoretical amount required to provide monolayer coverage of the aluminium flake.
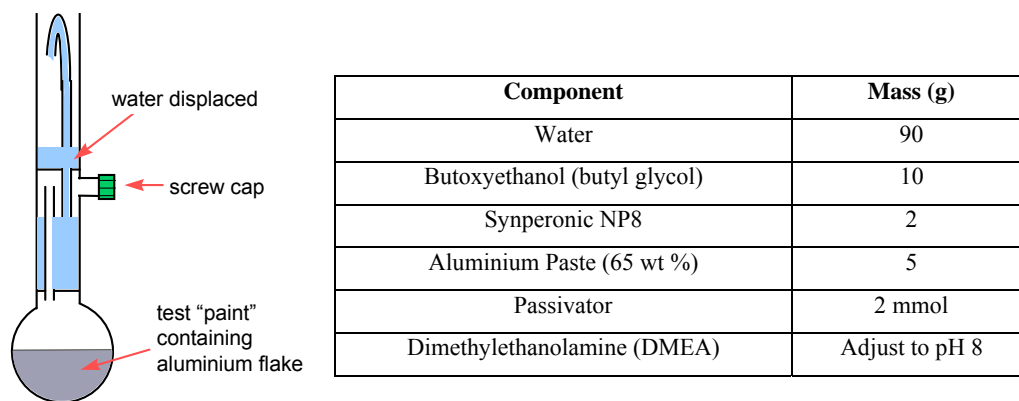

Component	Mass (g)
Water	90
Butoxyethanol (butyl glycol)	10
Synperonic NP8	2
Aluminium Paste (65 wt %)	5
Passivator	2 mmol
Dimethylethanolamine (DMEA)	Adjust to pH 8

Figure S1: The apparatus used to measure hydrogen evolution and the composition of a mixture used to represent an aqueous paint containing Al-flake.

XPS Experiments

XPS experiments were performed on a goethite sample stirred with a 0.002M solution of (**2**) ([Co(dien)Cl$_3$]) for 2 hours at 25 °C. The resulting signals were right on the detection limit of XPS, which meant that the much lower uptake onto ATH could not be studied using this technique. The strong Auger signal from the large amount of iron in the goethite sample obscured the cobalt signal in the desired region of the spectrum at approximately 800 eV, meaning the fingerprint region had to be used to confirm the presence of cobalt at approximately 70 eV. This precluded any quantitative analysis, and as such the ratio of Co:N could not be calculated. Nevertheless, the presence of cobalt and nitrogen, and the absence of chlorine, provides good evidence for the uptake of the complex in the proposed manner.

1. P. H. Crayton, *Inorg Syn*, 1963, **7**, 207-213; E. Kimura, S. Young and J. P. Collman, *Inorg Chem*, 1970, **9**, 1183; M. S. Okamoto and E. K. Barefield, *Inorg Chim Acta*, 1976, **17**, 91-96; J. Springbørg, C. E. Schäffer, J. M. Preston and B. Douglas, *Inorg Syn*, 2007, 63-77.

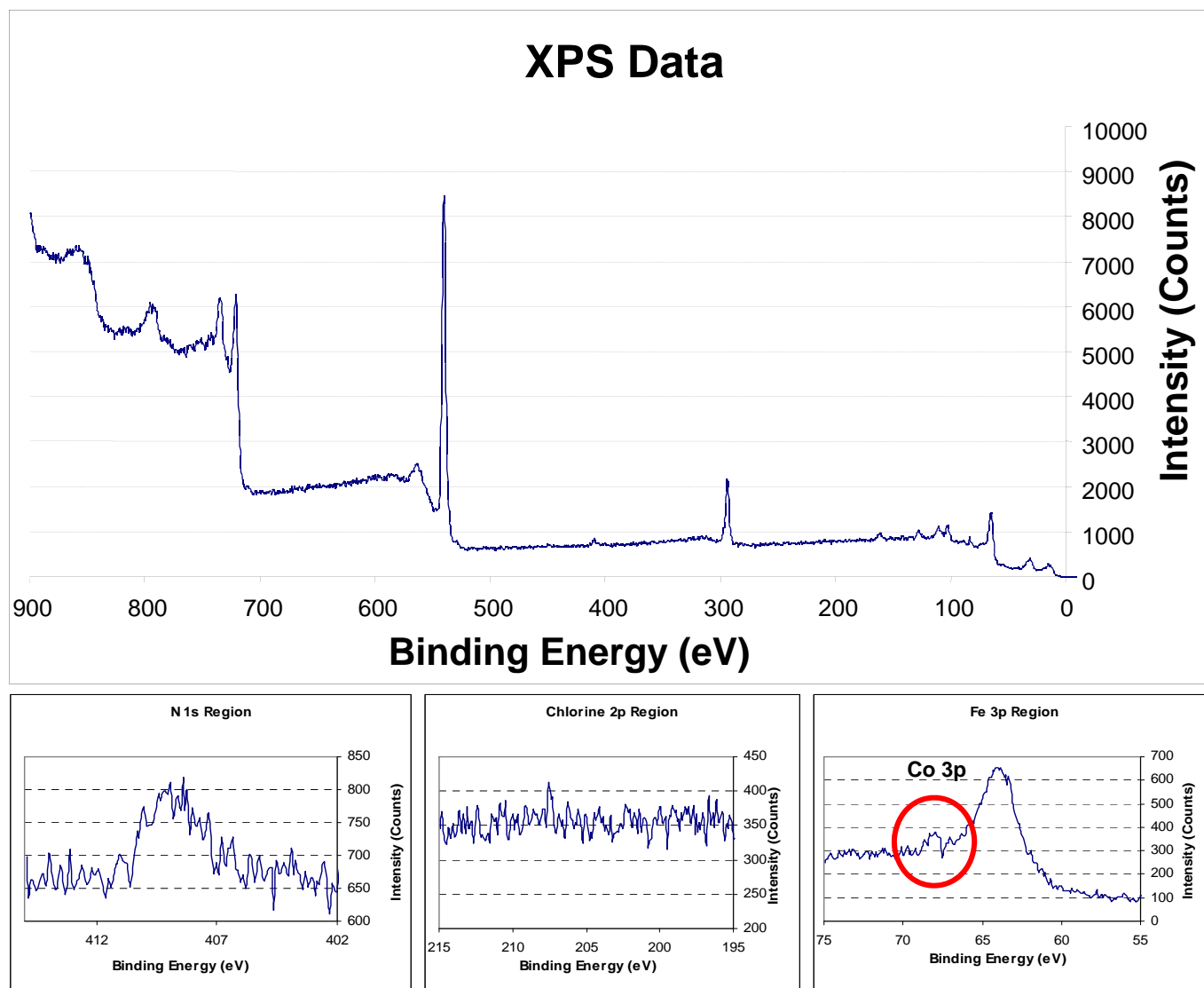2. P. G. Wight, *Internal Report*, Fujicolour, Blackley, UK M9 3ZS.

XPS Data

Binding Energy (eV)

Intensity (Counts)

| N 1s Region | Chlorine 2p Region | Fe 3p Region |

Co 3p

Binding Energy (eV)

Figure S2: XPS spectrum of a goethite substrate treated with a 0.002M solution of (**2**) ([Co(dien)Cl$_3$]) for two hours at 25 °C. Also shown are expansions of some relevant regions. Note that the signals from the species of interest are right on the detection limit of the XPS technique.

(1) [Co(tacn)Cl$_3$]
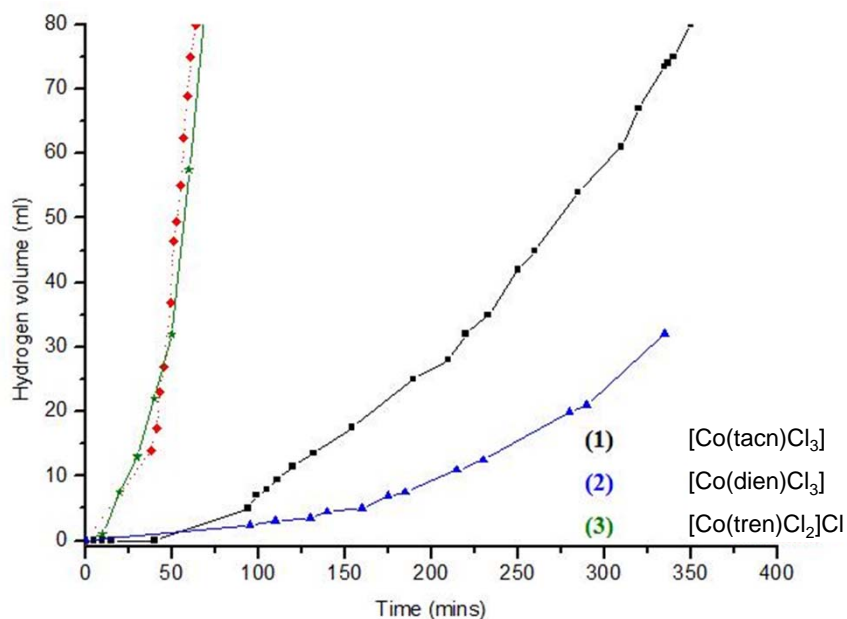**(2)** [Co(dien)Cl$_3$]
(3) [Co(tren)Cl$_2$]Cl

Figure S3: Hydrogen evolution from a simulated waterborne paint formulation containing aluminium flake to which complexes 1, 2 or 3 has been added.