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The Concentration and Selective Extraction of Copper(II), Rhodium(III), and Iridium(III) using a Copolymer Functionalised with Dithiocarbamate Groups. Spectroscopic Evidence for the Nature of the Binding Sites

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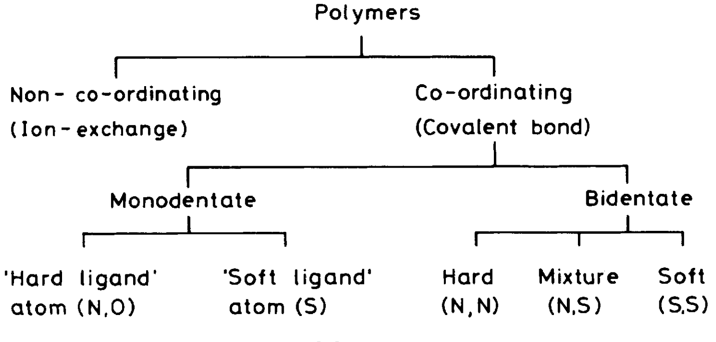
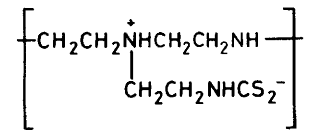
The use of the water-insoluble dithiocarbamate copolymer (**1**) ('PIED') as a reagent for the concentration and separation of rhodium, iridium, and copper has been investigated. The copolymer is able to separate iridium and rhodium, giving a separation ratio of up to 80 in unacidified solutions, and 5 in strong acid (4 mol dm^{-3}) solutions and to concentrate both rhodium(III) and copper(II). The selectivity ratio (Rh/Cu) of up to 9.8 is much less than expected and both metals are partially eluted by water. Spectroscopic properties of the metal–polymer complexes have been monitored and compared with those of model complexes and with those of a Cu^{II}-exchanged copolymer (**2**) ('IR-$45CS_2H$') which has a CuS, chromophore. At low loading (1%) the preferred site is five-co-ordinate but at higher loading the co-ordination appears to be CuS_2N_2 and is a model for 'blue' copper proteins. The ligand-field strength of the CS_2^- groups in (**1**) is significantly lower than expected, which is ascribed to strain in the polymer backbone causing weaker M–S bonds and accounts for the ease of elution of the metals. The poor selectivity of (**1**) for Ru^{III} over Cu^{II} is due to two factors: the rhodium and copper co-ordinate to different sites, and the co-ordination of rhodium limits the sites available to copper.

In previous papers we showed that copolymers which have been functionalised with dithiocarbamate groups may be used to concentrate and separate metals; the metals considered were cobalt and iron,[1] rhodium and iridium,[2] zinc and cadmium.[3] Appreciable quantities of both rhodium and copper are left in the platinum raffinate solution[4] (the solution which is left after the removal of platinum by solvent extraction). The solution is dilute (*ca.* 0.5—1.0 g dm^{-3} of Rh^{III} and *ca.* 0.5—2.5 g dm^{-3} of Cu^{II}) and a concentration process for rhodium is desirable. In the process in which a co-ordinating copolymer is used, it is necessary for the copolymer to be selective for rhodium as it would be uneconomic if Cu^{II} were co-extracted. It has been found useful to classify polymers according to Scheme 1. 'Co-ordinating polymers' are taken to mean those which are able to form a bond which has a marked degree of covalent character with a metal. In the particular case of the title copolymer (**1**) ('PIED') the dithiocarbamate groups might be expected to be strong chelating, bidentate (SS) ligands and hence capable of forming strong bonds with platinum group metals which would enable the copolymer to act as a scavenging reagent. We were hoping for separation ratios Rh/Cu > 1 000 because of the known high capacity of the copolymer (**1**) for Rh and Ir.[2] In addition to these groups there are nitrogen-containing groups which can be seen in the idealised repeating unit of Scheme 2. Part of the repeating unit of the copolymer (**2**) ('IR-$45CS_2H$'), a 4% cross-linked dithiocarbamate derivative of polystyrene-bound tripropylamine, is shown in Scheme 3 (not all the amine groups in every part of the copolymer may have been substituted by CS_2H).

Copolymer (**1**) is prepared from poly(etheneimine) which, in this case, had an average molecular weight of 40 000 and is highly branched with an average ratio of primary:secondary: tertiary groups of 1:2:1.[5] The dithiocarbamate groups are thought to be principally attached to the primary amine groups and it is possible that the metals are bonded to the nitrogen groups as well as (or in place of) the dithiocarbamate groups. Copolymer (**1**) is a powder and we have noted in a previous paper that Ag^+ can be partially (20%) eluted with water from a

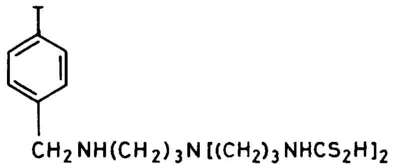


Scheme 1.



$$\left[\begin{array}{l} -CH_2CH_2\overset{+}{N}HCH_2CH_2NH- \\ \qquad\qquad | \\ \qquad\qquad CH_2CH_2NHCS_2^- \end{array}\right]$$

Scheme 2. Repeating unit of the copolymer (**1**)



Scheme 3. Part of the repeating unit of the copolymer (**2**)

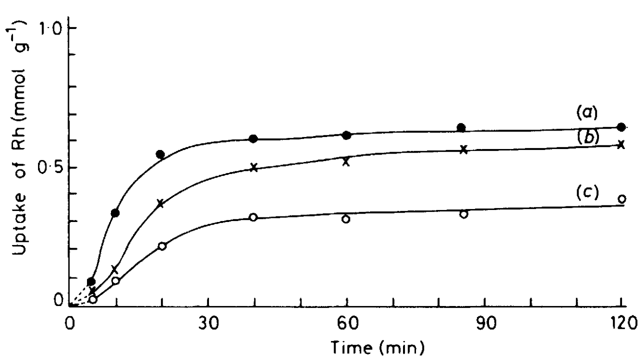


Figure 1. Rate of extraction of Rh by (**1**) as a function of particle size: (*a*) 150—250, (*b*) 250—500, (*c*) > 500 × 10^{-6}m (mesh)

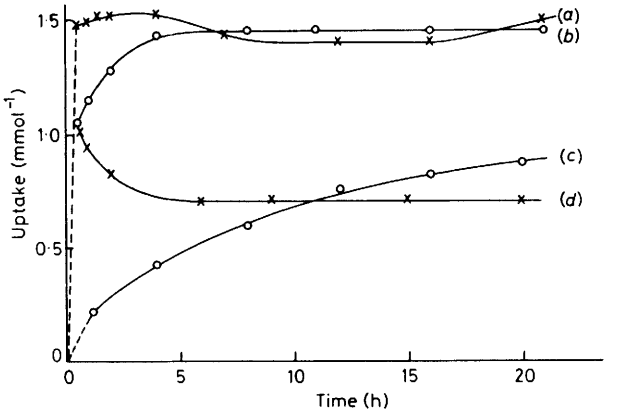


Figure 2. Rate of extraction of metals by (**1**) (mmol per g of dried copolymer); (*a*) Cu (no HCl added), (*b*) Rh, (*c*) Rh (no HCl added), and (*d*) Cu

powdered thiol copolymer;[6] it was important to determine whether there was similar leaching of metals from (**1**), as this could lead to loss of precious metal.

Experimental

Materials.—The copolymer (**1**) was prepared by the method of Giwa and Hudson[1] except that methanol was used in place of ethanol. The sulphur content of the products varied from 18 to 23% but for each experiment (*e.g.* Figure 1) the copolymer from the same preparation was used. The dithiocarbamate (**2**) from IR-45 (a commercial ion-exchange resin from Rohm and Haas) was prepared by the method of Kobayashi *et al.*[7] (Found: S, 11.7, 11.8. Calc. for $CHCH_2C_6H_4{\cdot}CH_2NHCH_2CH_2NHCS_2H$: 11.5%; this implies that a large proportion of the amine groups are functionalised). All the materials were obtained as lemon-yellow powders. Like many polyelectrolytes, (**1**) is more stable in the form of a salt rather than the acid form, which slowly decomposes to a yellow substance. However, the dithiocarbamate (**2**) appears to have an acceptable stability.

Physical Measurements.—Electronic reflectance spectra were measured on Beckman 2A and Unicam SP 1800 spectrophotometers against barium sulphate as reference. E.s.r. spectra were recorded on Varian E-3 and E-9 spectrometers using standard low-temperature equipment and diphenylpicrylhydrazyl as external calibrant.

Results and Discussion

Extraction of Rhodium(III) *and Copper*(II).—The precious metals are usually refined in strong acid media (4—6 mol dm^{-3} HCl) but at the stage when rhodium is extracted from the platinum raffinate it is possible partially to neutralise the solution if this aids separation. The use of the copolymer (**1**) as a scavenging reagent for rhodium, iridium, and copper was studied as a function of the particle size of the powder (Figure 1) and of the acid concentration. The solution of $[RhCl_6]^{3-}$ was boiled in 6 mol dm^{-3} HCl for 1 h to ensure that the concentrations of aqua-species were minimised. The rate and capacity of copolymer (**1**) for rhodium is dependent on the available surface area of the bead. The metal forms covalent bonds with the dithiocarbamate and cross-links the copolymer near to the surface and prevents further diffusion. Even so, the rate of extraction of rhodium(III) by the copolymer is rapid compared with existing commercial reagents.[8] Both copper(II) and rhodium(III) are extracted by (**1**). Clearly, more copper (1.5 mmol g^{-1}) is extracted in neutral solution than in acidic solution (1.05 mmol g^{-1}) (Figure 2). The rates of extraction in both media are acceptable ($t_{\frac{1}{2}} < 5$ min) but whereas there is little loss of copper from Cu–(**1**) in neutral solution, approximately 30% is eluted from the corresponding Cu–(**1**) in an acidic medium. In the case of rhodium(III), there is a slower rate of removal from the neutral solution and the capacity (0.91 mmol g^{-1} after 24 h) is lower when compared with the acidic solution (1.44 mmol g^{-1}). This is probably due to the slower rate of substitution of aqua-groups (unacidified solution) than the chloro-groups which are present in the strongly acidic solution.[9]

In solutions which contain both metals, rhodium extraction in the acidic medium is depressed (0.64 mmol g^{-1}) so that the selectivity coefficient for Rh/Cu is *ca.* 2.56 (Figure 3). Since rhodium extraction is also depressed in the neutral solution, but that for copper is unchanged, copolymer (**1**) does allow some separation of the two elements. In practice, the selectivity coefficient does change with acidity such that the maximum selectivity occurs at *ca.* 3 mol dm^{-3} HCl, but the value of the separation ratio Rh/Cu = 2.6 is much lower than the figure (*ca.* 1 000) anticipated. However, since the extraction rates of the metals were so encouraging, it was decided to see whether there was any extraction when (**1**) was used as a filter bed. To do this, a mixed solution of rhodium(III) and copper(II) (the concentration was approximately 150 g dm^{-3} for each as metal in 6 mol dm^{-3} HCl) was passed through a thin (0.5 cm) layer of the copolymer and rhodium(III) (87%) and copper(II) (40.5%) were extracted, giving a selectivity of Rh/Cu = 9.8 (*cf.* 2.6 above). The extraction of the two metals was studied on a small pilot plant such that 12 dm^3 of a solution which contained 25 g

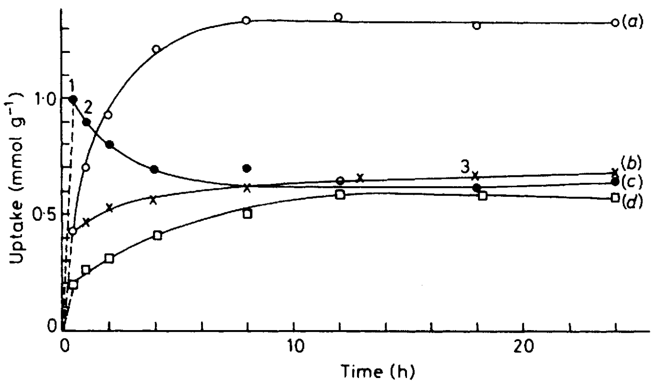


Figure 3. Competitive extraction of copper and rhodium: (*a*) Cu (no added acid), (*b*) Rh, (*c*) Cu, (*d*) Rh (no added acid)

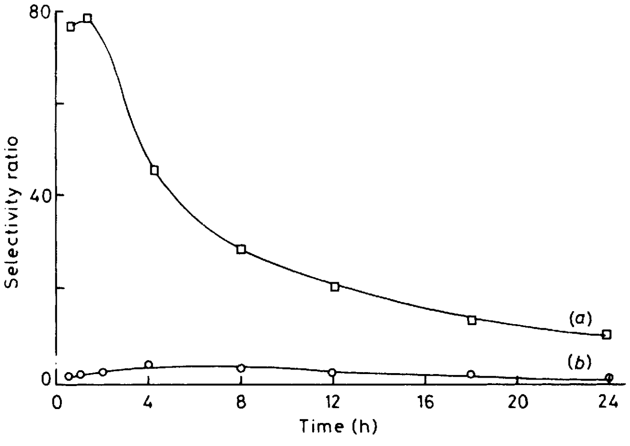


Figure 4. Selectivity for iridium over rhodium: (*a*) not acidified, (*b*) in 4 mol dm^{-3} HCl

dm^{-3} of the two metals as chloro-anions was stirred in a batch extractor with the copolymer. The rapid rates of extraction and good loading characteristics evident in the laboratory-scale tests (Figure 3) were also observed, but again the selectivity of (**1**) for rhodium was poor. Also disappointing was the fact that up to 40% of the copper was slowly eluted by water from the filter bed. In addition, rhodium (up to 10%) could also be eluted.

Separation of Rhodium and Iridium.—Hitherto the use of (**1**) as a selection reagent for rhodium over copper has been emphasised, but it can be used to give acceptable selectivities between the precious metals rhodium and iridium themselves. Although the iridium is present in solution as iridium(IV) and iridium(III) the metal appears to be extracted only as iridium(III).[2] In Figure 4 it can be seen that iridium is more rapidly extracted than rhodium, particularly from a solution to which no acid has been added. In such a solution, the metals are present as mixed chloro–aqua-species and it appears that the aqua groups are more readily substituted for iridium than for rhodium.[9] Consequently, acceptable separations can be achieved using unacidified solutions and contact times of up to *ca.* 1 h. This selectivity is not apparent in freshly prepared solutions which have been boiled in 6 mol dm^{-3} HCl, as the metals are present partially as the hexachloro-species. This selectivity, which depends upon a co-ordinative mechanism in which the dithiocarbamate groups form bonds with significant amounts of covalent character, illustrates that on some occasions co-ordinating polymers are more selective than ion-exchangers.

Spectroscopic Properties.—The unexpectedly small difference in selectivity between rhodium and copper, together with the rather easy elution of the loaded materials by water, prompted a spectroscopic study to ascertain what changes occurring in metal ion geometry at the binding site(s) are responsible for the 'ion-exchange co-ordination' properties of the copolymer.

Divalent metal ions. Copolymer (**1**) contains two different potentially co-ordinating groups namely the dithiocarbamate and the amine groups. The basic problem is thus to differentiate between the various possible species, *i.e.* CuS_4, CuS_4N_x ($x = 1$ or 2), CuN_3S, *etc.*, recalling that Cu^{II} gives a very 'plastic' co-ordination sphere[10] and that model, low-molecular-weight dithiocarbamates rarely co-ordinate to transition metal ions (and never, to the best of our knowledge, to Ni^{II} and Cu^{II}) in a monodentate fashion.[11]

Single-crystal studies of $[Cu(S_2CNEt_2)_2]$ itself, which has a CuS_4S square-based pyramidal geometry, have given the parameters $g_{\parallel} = 2.126$, $g_{\perp} = 2.027$, with $A_{\parallel} = 147.5$ G.[12] The changes in these parameters which occur when Cu^{II} is doped into the Ni^{II} and Zn^{II} analogues are believed to be due to the fact that the Cu^{II} adopts the square-planar geometry of the former and the approximately trigonal-bipyramidal geometry of the latter. Subsequent work with other diluent matrices has confirmed that all-sulphur co-ordination gives rise to very low g values because of π-bonding effects.[13] Although a CuN_2S_2 chromophore is also known to give low $g_{\parallel}$ values, again from single-crystal studies on complexes of known structure, the e.s.r. spectrum is now expected to be rhombic in character and the electronic spectrum to be distinctly different in having the major *d–d* band at lower energy (19 000 cm^{-1})[14] than that in $[Cu(S_2CNEt_2)_2]$ (*ca.* 22 000 cm^{-1}).[15,*] A choice between the two cases should therefore be possible.

The first point of note in the e.s.r. spectra (Figure 5) is that all give clear, single signals, with developed fine structure. The result shows that during loading there is no contamination by the $[CuCl_4]^{2-}$ present in the medium, and we are indeed dealing with well defined specific sites involving S,N-co-ordination and not with simple adsorption phenomena. In addition, in no case were $M = +1, +2$ transitions observed, nor was there any evidence for half-field lines.[16] The e.s.r. spectra are therefore caused by 'monomeric' type moieties.

The spectrum of Cu^{II}–(**2**) allows the clearest assignment of ligand type and geometry, giving a signal with fine structure even on $g_{\perp}$. All the parameters are in the range for low-molecular-weight dithiocarbamates, being particularly close to those for Cu^{2+} doped into $[Zn(S_2CNEt_2)_2]$[12] (see Table 1), especially as regards the more diagnostic $g_{\parallel}$ value (2.126). This is evidence for the presence of a rather distorted CuS_4S moiety in this low-loaded copolymer, *i.e.* the dithiocarbamate groups are bonding in the normal bidentate fashion. The electronic spectrum supports this donor-ligand and geometry assignment; bands are clearly visible at 16 000 and 21 800 cm^{-1} [Figure 6(*a*)]. {These energies may be compared with those of 15 600 ± 600 and 22 000 ± 300 cm^{-1} for $[Cu(S_2CNR_2)_2]$ (R = alkyl) complexes.[15]} The u.v. part of the spectrum is also very similar to that of $[Cu(S_2CNR_2)_2]$ complexes.[15] There are small, but significant changes in $g_{\parallel}$ and $A_{\parallel}$ (but not in the band shape, which remains pseudo-axial) at liquid-nitrogen temperature. These are in the sense of a very slight distortion of the donor atoms out of the CuS_4 plane (see below).

The e.s.r. spectra of both low- and high-loaded Cu^{II}–(**1**) pose more of a problem because in neither case is the spectrum

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[*] T. R. Reddy and R. Srinivasan (*J. Chem. Phys.*, 1965, 43, 1404) assign a band at 23 000 (*xy* polarised) to the $^2B \longrightarrow {}^2E$ transition and a band at 36 000 cm^{-1} to the $^2B \longrightarrow {}^2B_2$ transition.

Table 1. E.s.r. spectra data of Cu^{II}-loaded materials

Material	$g_{\parallel}$	$g_{\perp}$	$10^{-4}A_{\parallel}/\text{cm}^{-1}$	$10^{-4}A/\text{cm}^{-1}$
Cu^{II}–(**1**) (high-loaded)	2.236(3)	2.074(3)	104	—
Cu^{II}–(**1**) (low-loaded)	2.209(3)	2.065(3)	154(2)	
Cu^{II}–(**2**) (room temperature)	2.125(2)	2.025(2)	147(1)	15
Cu^{II}–(**2**) (77 K)	2.135(2)	2.025(2)	156(1)	14
Cu^{II}/Rh^{III}–(**1**) (low-loaded)				
Cu^{II}/Rh^{III}–(**1**) (high-loaded)	2.206(2)	2.062	166(2)	—
Cu^{II}/Rh^{III}–(**1**) (after 1 h loading)				
site a	2.255	—	150	
site b	2.231	—	112	
site c	1.83	—	90	
Cu^{II}/Rh^{III}–(**1**) (after 5 min loading)	2.262	—	140	

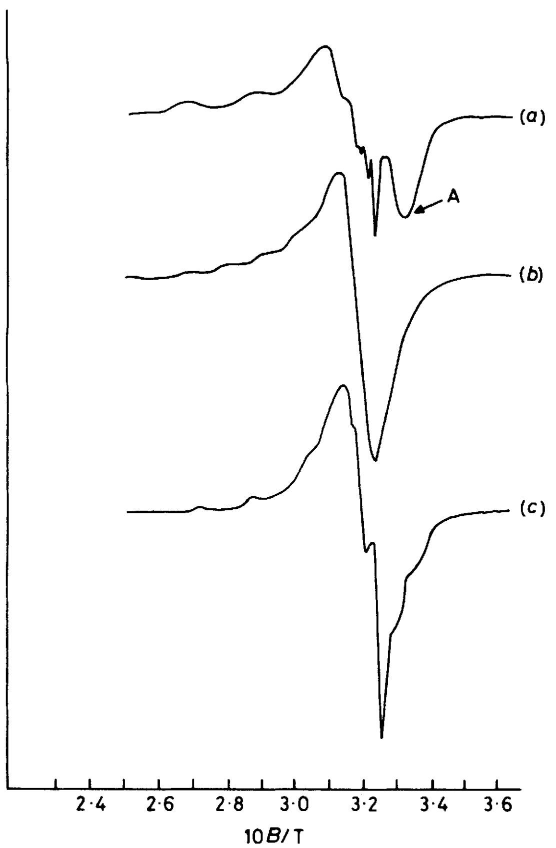

Figure 5. X-Band e.s.r. spectra of Cu^{II}-loaded materials: (*a*) 2—4% Cu^{II}–(**2**) [A denotes the 'overshoot' line characteristic of bis(dithiocarbamates)], (*b*) *ca.* 15% (**1**)–Cu^{II}, (*c*) 1—2% Cu^{II}–(**1**). All spectra recorded at 77 K

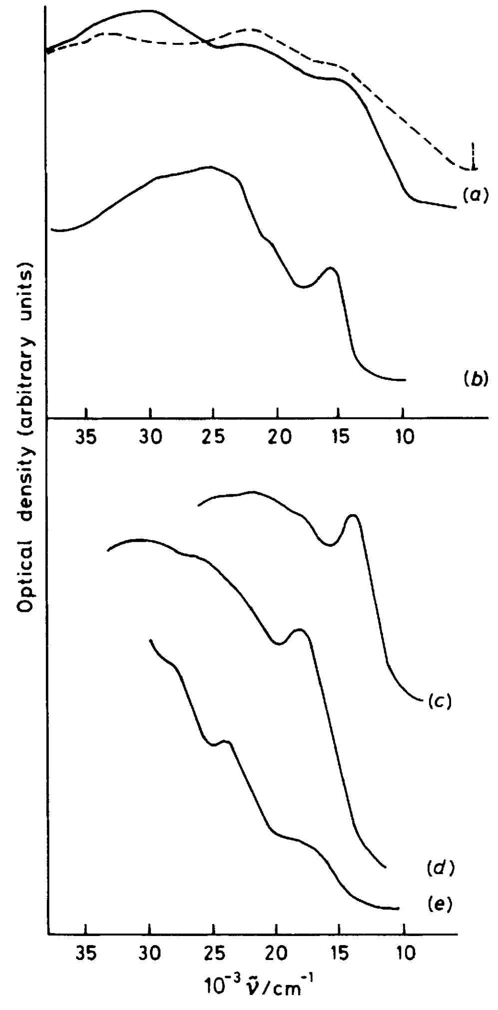

Figure 6. Electronic reflectance spectra: (*a*) (· · · ·) 15% Cu^{II}–(**1**), (——) 1—2% Cu^{II}–(**1**); (*b*) 10% Ni^{II}–(**1**); (*c*) 12% Co^{III}–(**1**); (*d*) 15% Rh^{III}–(**1**); (*e*) 15% Ir^{III}–(**1**)

obviously characteristic of a chromophore containing all-sulphur donors and in the low-loaded case unusual parameters are found, which are not found in low-molecular-weight analogues. In the high-loaded material, the criterion for a 'normal' e.s.r. signal, $g_{\parallel} > g_{\perp} > 2.02$ is fulfilled. Consequently, we can exclude geometries giving a d_{z^2} ground state (*i.e.* trigonal bipyramidal, compressed octahedral, *cis*-octahedral[16]). Particularly striking is the presence of a very low $A_{\parallel}$ parameter. The two pieces of information strongly suggest that a pseudo-tetrahedral geometry is involved. It has been known for some time that very low $A_{\parallel}$ values are diagnostic of this geometry and there have been many attempts to correlate dihedral distortions in an originally square-planar Cu^{II} moiety with $A_{\parallel}$,[17] with $g_{\parallel}$[18] (known also, from both experimental work and crystal-field calculations[19] to be sensitive to distortion towards a tetrahedron) and with the energy of the *d*–*d* transition due to d_{xy}, $d_{xz,yz}$, which moves to lower energy as the dihedral angle increases.[20] The presence of both a distinct low-energy shoulder in the electronic spectrum (Figure 6, Table 2) and a $g_{\parallel}$ value much higher than in (**2**) provide further support for a pseudo-tetrahedral formulation. Indeed, following the interpolations of

Table 2. Electronic reflectance spectral data (10^3 cm^{-1})

Material	*d–d* Bands	Intra-ligand and c.t.
$\mathrm{Cu^{II}}$–(1) (low-loaded)	15.3 (sh), 22.2	29.4, 33.0 (sh), 38.8 (sh)
$\mathrm{Cu^{II}}$–(1) (high-loaded)	9.5 (sh), 15.4, 22.2	33.3, 38.0 (sh)
$\mathrm{Cu^{II}}$–(2)	16.0, 22.0 (vbr)	33.4 (sh)
$\mathrm{Ni^{II}}$–(1)	15.8,20.6 (sh)	23.15, 25.3, 29.4, 33.3, 40.0
$\mathrm{Co^{III}}$–(1)	14.82, 18.87	23.10, 37.04
$\mathrm{Rh^{III}}$–(1)	19.40, 25.60	30.77, 39.20
$\mathrm{Ir^{III}}$–(1)	18.5, 23.80, 27.40	

Yokoi and Addison[18] from $A_{\parallel}$ *versus* $g_{\parallel}$ plots for varying donor ligands, the parameters obtained are in line with a $CuSN_3$ or CuS_2N_2 moiety (more strictly the former than the latter, but the $A_{\parallel}$ *versus* $g_{\parallel}$ curves for sulphur-containing ligands were interpolated from those for other donor-atom groups, so a clear distinction between the two is not possible).

If we then use the $g_{\parallel}$ *versus* dihedral angle plots[18] a dihedral angle of *ca.* 70° is derived. This is of the same order as found in the 'blue' proteins (*e.g.* plastocyanin has $A_{\parallel} = 64$ and dihedral angle of 80°[21]). A similar value (to within ±2°) is arrived at by interpolation of the $A_{\parallel}$ value for plastocyanin and using $A_{\parallel} = 187 \times 10^{-4}$ cm^{-1} as the 'square-planar benchmark.' This is in agreement with work by Bereman *et al.*[22] in which a decrement of 3.5 cm^{-1} per degree was suggested. However, this agreement might be fortuitous because the assumption was made that $A_{\parallel}$ varied linearly with dihedral angle but on the basis of only two points derived from crystallographically known CuS_2N_2 moieties.[22]

At very low loading, the e.s.r. spectrum is considerably different, demonstrating that (at least) two different sites are available for Cu^{2+} in (1). The $A_{\parallel}$ parameter is no longer attributable to a pseudo-tetrahedral geometry, and the spectrum is rhombic in type. Using the more recent extensive correlations of Addison *et al.*[23] for mixed S,N,O-donor ligands indicates that the low-field A and g parameters are as expected for a CuS_3N_2 chromophore. Unfortunately, ambiguity remains in this geometry assignment because the high-field part of the spectrum appears to consist of a $g_{\perp} = 2.00$ line, not easy to explain using the standard methods.[16] [Neither alternative explanation, *i.e.* (*i*) the high-field signal is due to impurity ion, or (*ii*) it is due to a second site with a d_{z^2} ground state, is satisfactory. If (*i*) were the case, both e.s.r. and electronic spectra would be expected to be much lower in intensity, this is not so. Conversely, the band shape is not as expected for a d_{z^2} type ground state, nor is the electronic spectrum convincingly that of a trigonal-bipyramidal moiety.[24]]

Compounds of Nickel with (1).—The question remains as to whether the above geometries are obtained because of the configuration of the polymer or do they result from the plasticity of the $\mathrm{Cu^{II}}$ co-ordination? The electronic spectrum of $\mathrm{Ni^{II}}$–(1) throws some light on this point. Fully loaded $\mathrm{Ni^{II}}$–(1) has been reported to be paramagnetic and to give an electronic spectrum diagnostic of both square-planar (diamagnetic) + octahedral (paramagnetic) moieties present in the proportion 2:1.[25] On re-measuring the spectrum (Figure 6) it is seen that the rich spectral details can be readily assigned to a NiS_4 chromophore (the minor octahedral component having much weaker bands). The spectrum is virtually superposable on that of $[Ni(S_2CNH_2)_2]$[22] throughout the whole of the spectral range, including intra-ligand bands. A correlation is known to exist between Ni–S bond length and the energies of the $d_{x^2-y^2}$, d_{z^2}, and d_{xy} transitions, from which we interpolate a Ni–S bond length of *ca.* 2.2 Å.[26] These results show that the dithiocarbamate groups in (1) are capable of giving a regular, square-planar MS_4 group.

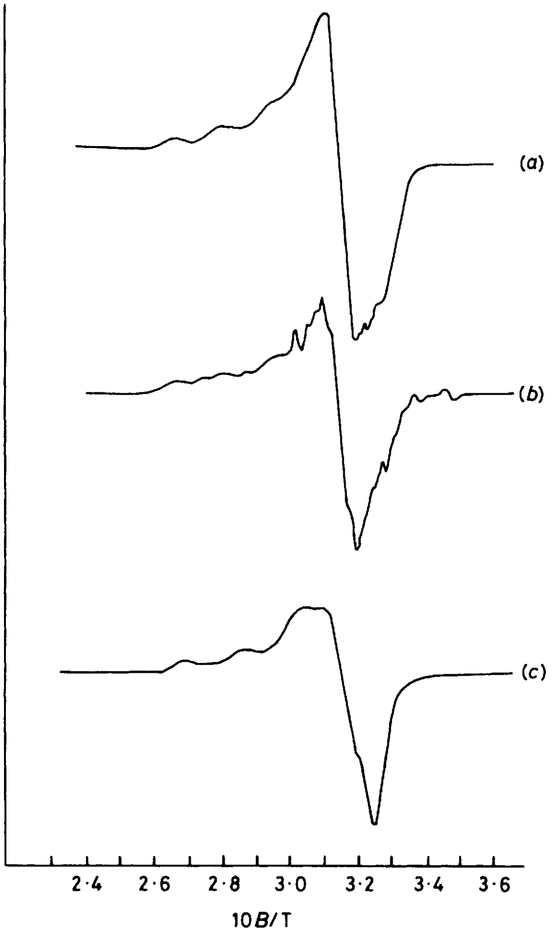

Figure 7. E.s.r. spectra of $\mathrm{Cu^{II}/Rh^{III}}$–(1): (*a*) after 5 min contact, (*b*) after 1 h contact, (*c*) after complete loading; (*a*)—(*c*) correspond to points 1—3 respectively of Figure 3

Trivalent Metal Ions.—The secondary amine groups in (1) are expected to be of similar ligand-field strength as those present in ethylenediamine (en), and it is known that MN_6 chromophores (M = $\mathrm{Co^{III}}$, $\mathrm{Rh^{III}}$, or $\mathrm{Ir^{III}}$) give *d–d* spectra with bands at significantly higher energy than those expected for all-S-bonding dialkyldithiocarbamates.[26] Thus $[Co(en)_3]^{3+}$ gives a *d–d* spectrum with the first spin-allowed band at 23 200 cm^{-1}, $[Rh(en)_3]^{3+}$ one with the first *d–d* band at 33 220 cm^{-1}, and $[Ir(en)_3]^{3+}$ one with the first spin-allowed band at 41 000 cm^{-1}.[27] In addition, the presence of mixed co-ordinations MN_xS_{6-y} would be expected to lead to some observable splitting of these triply degenerate levels.[28] It should therefore be possible to distinguish between the different chromophore groups which may arise when the polymer co-ordinates to these metal ions. This is indeed the case, despite the presence of very close intense charge-transfer (c.t.) transitions in the near-u.v./u.v. region (see Figure 6). The observed bands lie in the range expected for all-S bonding.[11] However, they are at significantly lower energies than those in low-molecular-weight analogues.[11,29] Indeed, they are close to those for $(RS)_2PS_2H$ and R_2PS_2H (R = alkyl), known to give significantly longer M–S bond lengths.[30] This is direct evidence that the backbone configuration in (1) induces strain into the MS_6 moiety.

Site Availability during Competitive Loading of Cu^{II} *and* Rh^{III}.—During competitive loading, the e.s.r. spectra of the materials loaded at the beginning, after 1 h of loading, and at the end of the loading, *i.e.* at points 1, 2, and 3 of Figure 3, are different. After 5 min equilibration, the signal is still ascribable to the same moiety as present in the low-loaded Cu^{II} alone. However, the $g_{\parallel}$ and $A_{\parallel}$ parameters are distinctly different (Figure 7). The same signal is still present after 1 h contacting of mixed Cu^{II} and Rh^{III} with (**1**), but there is a clear further signal having parameters close to those in 1—2% Cu^{II}–(**1**). A third signal is also present, with even more unorthodox parameters: $g_{\parallel} < g_{\perp} \ll 2.00$ and $A_{\parallel} = 90 \times 10^{-4}$ cm^{-1}, and an electronic spectrum with no sign of low-energy *d–d* absorption[16] [the reflectance spectra were superpositions of the RhS_6 species and the 1—2% Cu^{II}–(**1**) moiety]. We can only speculate that a compressed-tetragonal or trigonal-bipyramidal geometry may be responsible. Whatever the case, this site has been induced by co-ordination of the Rh^{III} to the S_6 site. The appearance of this new site corresponds to the peak in Cu^{II} uptake (Figure 3), and this signal is no longer present in the e.s.r. spectrum of (**1**) after complete competitive uptake.

At no time was the signal attributed to a pseudo-tetrahedral CuS_2N_2 (or $CuSN_3$) site observed. This result suggests that the Rh^{III} has subtracted the major site for Cu^{II} binding, which would rationalise the decline in Cu^{II} uptake after 1 h.

Conclusions

We have shown that the copolymer (**1**) provides a good separation between Ir and Rh in unacidified solutions, but that the separation of Rh from Cu is poor and significant proportions of the metals are washed out even by water. The selectivity for Ir over Rh is related to easier replacement of co-ordinated aqua-groups on Ir than those on Rh. It is also related to the fact that Rh and Ir are competing for identical (S_6) sites. The poor selectivity of Rh^{III} over Cu^{II}[31] is related to the fact that PIED provides different sites for Rh and for Cu. Indeed, more than one site is available for Cu^{II} depending on whether Rh^{III} is present and on the degree of loading, *i.e.* Rh^{III} and Cu^{II} co-ordination is synergistic. This behaviour is not found in low-molecular weight analogues and it appears that 15%-loaded Cu^{II}–(**1**) is one of the closest models yet found for the 'blue' copper proteins.[32] The ease of elution is related to strain in the co-ordinated copolymer, which gives rise to weaker M–S bonds than those in low-molecular-weight analogues.

As far as we are aware, this is the first attempt to relate the separation of precious metals from base metals by co-ordinating polymers to co-ordination chemistry.

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