Electron Spin Resonance Studies of γ-Irradiated Hexacyanoruthenate(II) Ions in Various Host Lattices

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E.s.r. data for γ-irradiated hexacyanoruthenate(II) ions doped into various host lattices are reported. The main complexes formed are Ru^I species (low-spin d^7), assigned as $Ru(CN)_4(CN')H_2O^{4-}$, $Ru(CN)_4(CN')_2{}^{5-}$, $Ru(CN)_4(CN')Hal^{5-}$, and $Ru(CN)_4(Hal)_2{}^{5-}$, where CN' indicates a cyanide ligand tilted off the z-axis. The magnitudes of the hyperfine coupling to ruthenium and nitrogen are used to discuss the structures of the complexes.

In a previous e.s.r. study,[1] several Fe^I species were identified as products from the γ-irradiation of hexacyanoferrate(III) ions in various host lattices. The analogous hexacyanoruthenate(II) ion is expected to act as an efficient electron trap in the environment of an $MX_6{}^{5-}$ unit that has been displaced from the host lattice (MX). We wished to investigate whether the analogous Ru^I species could be prepared and the factors governing the stability and formation of these $4d^7$ complexes. We also wished to study the magnitude of the coupling to ^{14}N and to halogen and, if possible, to detect hyperfine coupling to the odd isotopes, ^{99}Ru and ^{101}Ru ($I = 5/2$; 12·8 and 17% abundant respectively). Since this study was completed, data for species produced from the X- and γ-irradiation of the pure solid, $K_4Ru(CN)_6,3H_2O$, have been reported.[2]

EXPERIMENTAL

Doped samples were obtained by crystallisation of the alkali-metal halide from aqueous solutions containing

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[1] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Dalton*, 1973, 14.

[2] R. S. Eachus and F. G. Herring, *Canad. J. Chem.*, 1972, **50**, 162.

$K_4Ru(CN)_6$ in concentrations varying from 0·005 to 0·1 mol %. AnalaR reagents were used except for $K_4Ru(CN)_6$ which was the best grade available. Finely powdered samples were exposed to ^{60}Co γ-rays from a Vickrad source at a dose rate of *ca.* 4 Mrad h^{-1} for periods up to *ca.* 4 h. Experiments (A—D) were performed on each sample. A, irradiation at 77 K; B, annealing (A) to room temperature; C, irradiation at room temperature; and D, annealing (C) to between 400 and 500 K for several hours. N.B. Other variations on A—D gave the expected results.[3]

E.s.r. spectra for very finely powdered samples were recorded at 77 K on an *X*-band Varian E.3 spectrometer.

RESULTS AND DISCUSSION

In all cases we use $\parallel$ and $\perp$ symbols for the e.s.r. parameters because in no instance did the powder spectra indicate deviations from cylindrical symmetry. Unfortunately, we cannot judge from the powder spectra alone how accurately the *g*- and *A*-tensors are aligned together, and we have to assume that they are colinear. However, in the case of species 2N, studied in a single crystal of $K_4Ru(CN)_6,3H_2O$,[2] there was clear evidence for a slight deviation from colinearity.

Incorporation of Ions into the Lattice.—The hexacyanoruthenate ions were easily incorporated into KCl, KBr, NaCl, and NaBr but no incorporation could be detected in fluoride and iodide hosts.

Potassium Chloride Doped with Hexacyanoruthenate(II) *Ions.*—Low-temperature irradiation produced a broad e.s.r. triplet feature (species N) together with a quintet (species 2N) and the V_K-centre, Cl_2^-. Other features were observed between the perpendicular features of species N/2N and the free-spin *g*-value. Partial annealing to ambient temperatures caused an increase in the intensity of these extra features (assigned as species A and species B), whereas the Cl_2^- spectrum diminished and the triplet (species N) and surrounding shoulders became more clearly resolved. Species A and B are believed to be due to a manganese impurity in the lattice, since experiments involving potassium chloride doped with $Mn(CN)_6^{4-}$ produced much larger concentrations of these species.

Room-temperature irradiation produced species N with clearly defined multiplet shoulders at low and high field. A small amount of the dichloride (species 2Cl) was also detected, indicating that some of the lines in the shoulders around species N could be due to the monohalogenated species (N.Cl), although some of the lines are expected to arise from coupling to the ^{99}Ru and ^{101}Ru isotopes.

High-temperature annealing removed species N and excellent spectra of species N.Cl and 2Cl, were recorded (Figure 1). The satellite lines for the species 2Cl could then be analysed in terms of the odd ruthenium isotopes. However, for the N.Cl species only an upper limit for the ruthenium coupling could be estimated (see Table 1).

Sodium Chloride Doped with Hexacyanoruthenate(II) *Ions.*—Irradiation at 77 K produced the V_K-centre, Cl_2^-, together with a strong line (species C) and shoulders to low field (species N) and high field (species D). In some samples a broad free-spin feature was detected which exhibited a multiplet structure on annealing to room temperature. From the similarity of this spectrum to that of the free-spin feature in the KCl host we assign it as species B. On annealing, species C exhibited partially resolvable hyperfine structure, Cl_2^- decayed, and surprisingly, a septet, possibly a dichloro-species (species 2Cl) was observed at low field. (Di-halogenated species normally only appear after prolonged room-temperature irradiation and/or high-temperature annealing).

Room-temperature irradiation produced spectra comparable with those produced by low-temperature irradiation with subsequent annealing to room temperature.

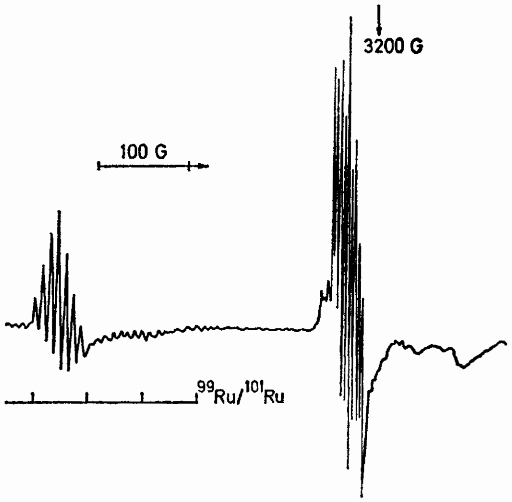

FIGURE 1 *X*-Band e.s.r. spectrum of a KCl host doped with hexacyanoruthenate(II) ions, showing features assigned to $Ru(CN)_4Cl_2^{5-}$ and $Ru(CN)_4(CN')Cl^{5-}$; the lines due to the odd ruthenium isotopes can be seen near the low field features of $Ru(CN)_4Cl_2^{5-}$

High-temperature annealing caused species C to disappear and the ^{14}N hyperfine structure of species N became resolved. The broad perpendicular features of the species assigned as species N.Cl were also observed. A septet assigned to the normal dihalogenated species (species 2Cl) appeared in the low-field region.

Potassium Bromide Doped with Hexacyanoruthenate(II) *Ions.*—Low-temperature irradiation produced the V_K-centre, Br_2^-, together with a perpendicular quintet feature (species 2N), with shoulders to low and high field, most probably due to the odd ruthenium isotopes. Annealing to room temperature caused species 2N to be replaced by species N(a) an intense triplet, and another lower intensity triplet just to low field species N(b).

Prolonged room-temperature irradiation produced a quartet of triplets (species N.Br) and a low-field septet, species 2Br, the triplet assigned to species N(a) being overshadowed by the intense N.Br spectrum. The e.s.r. spectra appear quite similar to those of the analogous Fe^I system but the derived parameters are quite different (see Table 1).

Sodium Bromide Doped with Hexacyanoruthenate(II)

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[3] M. C. R. Symons and J. G. Wilkinson, *J.C.S. Dalton*, 1972, 1086.

Ions.—Low-temperature irradiation produced the V_K-centre, Br_2^-, together with a perpendicular feature (species N) which could only be clearly identified when the Br_2^- spectrum decayed, on annealing to room temperature. There was also a multiplet structure (species E) to low field of species N but clear assignment was difficult.

On irradiation at room temperature for short periods, only species N was produced. Prolonged irradiation resulted in the appearance of a perpendicular quartet of lines (species N.Br) but the parallel features were very poorly defined. However, using data from previous studies[1,3] of these complexes [$g_{\parallel} = ca.\ 2{\cdot}0023$ and $A_{\parallel}$(Hal) $= ca.\ 3/2\ A_{\perp}$(Hal)] these features could be satisfactorily explained.

TABLE 1

E.s.r. data for species produced by γ-irradiation of $K_4Ru(CN)_6$ in various lattices

				g-Tensor		^{14}N Tensor		Hal. tensor		Ru hf tensor	
Host	Symbol	Postulated species	Treatment[a]	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$/G	$A_{\perp}$/G	$A_{\parallel}$/G	$A_{\perp}$/G	$A_{\parallel}$/G	$A_{\perp}$/G
KCl	2N	$Ru(CN)_4(CN')_2^{5-}$	A	*b*	2·078	*c*	*c*				
	N (a)	$Ru(CN)_4(CN')H_2O^{5-}$	A,B,C	1·998	2·077	*c*	3·6				
	N (b)	$Ru(CN)_4(CN')H_2O^{5-}$	A	*b*	2·084	*c*	*c*				
	N.Cl	$Ru(CN)_4(CN')Cl^{5-}$	C,D	1·998	2·076	*c*	3·75	*c*	8·5	*c*	$\leqslant 14$[d]
	2Cl	$Ru(CN)_4(Cl)_2^{5-}$	C,D	1·990	2·266			17·5	8·5	*c*	60·5
	A	Mn species[a]	A,B								
	B	Mn species[a]	A,B,C								
NaCl	2N	$Ru(CN)_4(CN')_2^{5-}$	A	*b*	2·065	*c*	*c*				
	N	$Ru(CN)_4(CN')H_2O^{5-}$	A	*b*	2·081	*c*	*c*				
	N.Cl	$Ru(CN)_4(CN')Cl^{5-}$	C,D	*b*	2·061	*c*	*c*	*c*	19		
	2Cl	$Ru(CN)_4Cl_2^{5-}$	D	*b*	2·194			*c*	18		
			(B,C	*b*	2·15				8·3)?[a]		
	C	Ru(I) species	A	*b*	2·065						
	D	Ru(I) species	A	*b*	2·044						
KBr	2N	$Ru(CN)_4(CN')_2^{5-}$	A	*b*	2·085	*c*	3·75				
	N (a)	$Ru(CN)_4(CN')H_2O^{5-}$	A,B,C	1·998	2·085	*c*	3·75				
	N (b)	$Ru(CN)_4(CN')H_2O^{5-}$	A,B	*b*	2·091	*c*	3·75				
	N.Br	$Ru(CN)_4(CN')Br^{5-}$	C,D	*b*	2·078	*c*	3·75	72	46		
	2Br	$Ru(CN)_4Br_2^{5-}$	C,D	*b*	2·244			*b*	50		
NaBr	2N	$Ru(CN)_4(CN')_2^{5-}$	A	*b*	2·076	*c*	*c*				
	N	$Ru(CN)_4(CN')H_2O^{5-}$	A	*b*	2·076	*c*	3·6				
	N.Br	$Ru(CN)_4(CN')Br^{5-}$	C,D	2·00	2·067	*c*	*c*	124	87		
	E	Ru(I) species	A	*b*	2·081						

		g-Tensor with respect to				Ru hyperfine tensor with respect to			
Host	Symbol	a	b	c[e]		a	b	c	
$K_4Ru(CN)_6,3H_2O$[f]	2N	2·0855	1·9982	2·0855	$A_{iso}(^{14}N) = 3{\cdot}0$	5·0	38·4	5·0	(^{101}Ru)
	N	2·0844	1·9984	2·0884	$A_{iso}(^{14}N) = 4{\cdot}5$	5·0	35·1	5·0	(^{99}Ru)

[a] See text. [b] Obscured by free spin features. [c] Unresolved. [d] Upper limit. [e] a, b, and c are crystallographic axes. [f] Ref. 2.

High-temperature annealing only weakened the signal intensity, although the triplet ^{14}N hyperfine structure of species N became resolved. No dibromo-species was observed, but as the noise level was high this does not preclude its formation.

Identification of Species.—Addition of an electron to the d^6 hexacyanoruthenate ion is expected to give an axially distorted, d^7, Ru^I complex. The form of the *g*-tensor for a d_{z^2} configuration (*i.e.* $g_{\perp} \gg g_{\parallel} = 2{\cdot}0023$) is exhibited by all the complexes produced (see Table 1). The magnitudes of the $g_{\perp}$ values are less than those for the corresponding Fe^I complexes, indicating that the value of λ/Δ has decreased. Since λ is greater for the 4*d* elements,[4] the value of $\Delta[= E_{d_{xz,yz}} - E_{d_{z^2}}]$ must have increased considerably.

Previous studies[5] have indicated that the $g_{\perp}$ values decrease as the number of ligands increases from four to six. We might expect that a species $Ru(CN)_5^{4-}$, analogous to $Fe(CN)_5^{4-}$ and $Co(CN)_5^{3-}$ would have a $g_{\perp}$ value of *ca.* 2·10, but no features in this region were observed. This may indicate a reluctance of Ru^I to form the five co-ordinate complex.

Species 2*N*. A perpendicular quintet, attributable to two equivalent nitrogen nuclei, was observed in the potassium halide hosts having $A_{\perp}$ (^{14}N) = 3·6 G, which is considerably greater than that for the analogous quintets of Fe^I [1,6] or Co^{II} [3,7] of *ca.* 2·0 G. Nevertheless, the value of 3·6 G is still very low for a ligand having nitrogen directly bonded to a metal, normal values being *ca.* 15 G (*cf.* d^7 nitrosyls[8] and d^9 phthalocyanines[9]). We postulate that the species giving rise to the coupling is $Ru(CN)_4(CN')_2^{5-}$, analogous to the Fe^I and Co^{II} complexes. Here CN′ represents a cyanide ligand, tilted off the *z*-axis and possibly shifted laterally as well. Using the data of Eachus and Herring[2] for this species, we calculate a central metal atom spin density of comparable size to that on cobalt(II) in the analogous complex. Analysis of the ^{14}N hyperfine data shows that the change in coupling is due to an increase in *s*-density of

[4] F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry 2nd edn., 1969, p. 911.

[5] M. C. R. Symons and J. G. Wilkinson, *J. Chem. Soc.* (*A*), 1971, 2069.

[6] K. D. J. Root and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 2366.

[7] J. Danon, R. P. A. Muniz, A. O. Caride, and I. Wolfson, *J. Mol. Structure*, 1967, **1**, 127.

[8] B. A. Goodman, D. A. C. McNeil, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1966, 1547.

[9] E. M. Roberts and W. S. Koski, *J. Amer. Chem. Soc.*, 1960, **82**, 3006; 1961, **83**, 1865.

ca. 0·3%, the anisotropy remaining small and similar to that for the cobalt(II) complex. We stress that the simple alternative of a complex with D_{4h} symmetry having two stretched M–CN bonds is not acceptable since normal cyanide ligands in such a complex are not expected to exhibit a detectable hyperfine coupling.

Species N. Although in previous studies [1,3] the ^{14}N hyperfine structure has been unresolved in sodium halide hosts, broad single lines being detected, the increased value of $A_{\perp}(^{14}N)$ allows resolution for the ruthenium complex in these hosts. The N species is formulated as $Ru(CN)_4(CN')X^{n-}$ where X is the ligand *trans* to the bent cyanide ligand, for similar reasons as above, and $n = 4$ or 5 depending on the nature of X. The hyperfine coupling to ^{14}N for species N was identical to that for species 2N. Eachus *et al.*[2] found a difference in these couplings, but only A_{iso} values were quoted. (The nature of ligand X is discussed below.)

Species N.Hal. The species exhibiting hyperfine structure from both ^{14}N and halogen in the potassium halide hosts are assigned as N.Hal. The broader lines assigned to this species in sodium halide lattices (Table 1) do not allow resolution of the ^{14}N hyperfine structure, but we see no reason for classing these species as anything other than $Ru(CN)_4(CN')Hal^{5-}$.

Species 2Hal. The species exhibiting hyperfine coupling to two equivalent halogen nuclei are formulated as the six-co-ordinate complexes, $Ru(CN)_4(Hal)_2^{5-}$, even though the $g_{\perp}$ value is unusually high.

Damage Mechanisms.—An exactly similar set of products are observed from the irradiation of hexacyanoruthenate(II) ions as were discovered for the irradiation of the analogous Fe^{II} system. In the discussion of the damage mechanisms for the hexacyanoferrate(II) system it was argued [1] that a small concentration of impurity ions [$Fe(CN)_5H_2O^{3-}$ or $Fe(CN)_4(H_2O)_2^{2-}$] were incorporated, with the hexacyanoferrate ion, and acted as more efficient electron traps until their concentration became so low that reaction with $Fe(CN)_6^{4-}$ ions to produce the $Fe(CN)_4(CN')_2^{5-}$ ion predominated. Since $Ru(CN)_5H_2O^{3-}$ has been postulated [10] as an intermediate in the hydrolysis of hexacyanoruthenate(II) ions, this would seem to be the best explanation for the present results also.

The results reported by Eachus and Herring [2] agree broadly with ours, but certain differences should be considered. Thus, in the low-temperature γ-irradiation of the pure solid, $K_4Ru(CN)_6,3H_2O$, only the 2N species was observed, but at room temperature only the N species was detected.[2] This can be explained in our theory if, in the pure crystalline solid, less of the $Ru(CN)_5H_2O^{3-}$ ion was present. Then the γ-ray doses were sufficient to cause major damage to the host material. However, the lower energy *X*-irradiation used at room temperature caused less damage, and preferential trapping by the $Ru(CN)_5(H_2O)^{3-}$ ions gave the N species predominantly.

Magnitude of $A(^{14}N)$.—Although Eachus and Herring [2] subscribe to Danon's theory [11] of isocyanide bonding, their single-crystal results are better in accord with our concept of tilted cyanide ligands. Our theory requires that two of the three principle directions of the ^{14}N tensors should differ from those for the *g*-tensors and ruthenium hyperfine tensors, and this was indeed observed by Eachus and Herring.[2] Unfortunately, the results were not reported in sufficient detail to enable us to deduce the relative directions of these tensors. The increase in $A(^{14}N)$ on going from the Fe^{I} and Co^{II} complexes to the Ru^{I} complex has arisen because of an increase (*ca.* 0·3%) in the *s*-orbital population on ^{14}N, the anisotropy remaining about the same. This small change may reflect a very slightly increased delocalisation, which might be expected,[12,13] but it may simply mean that the preferred degree of tilt of the CN′ ligand is slightly greater for the ruthenium complexes.

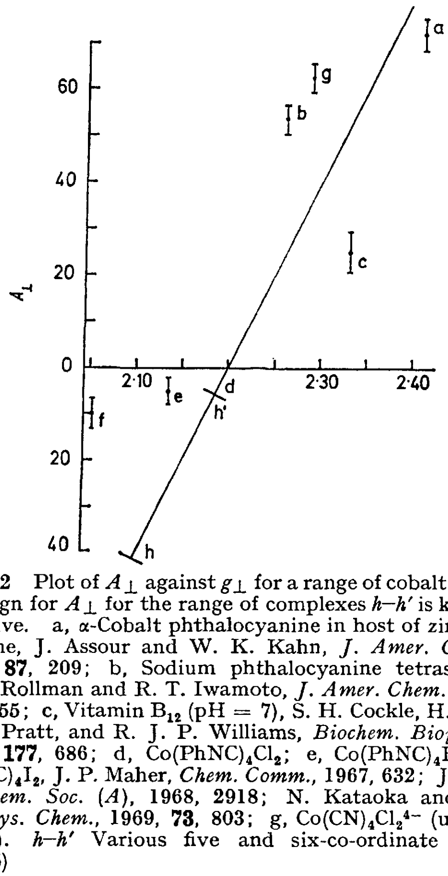

FIGURE 2 Plot of $A_{\perp}$ against $g_{\perp}$ for a range of cobalt complexes. The sign for $A_{\perp}$ for the range of complexes *h*–*h′* is known to be negative. a, α-Cobalt phthalocyanine in host of zinc phthalocyanine, J. Assour and W. K. Kahn, *J. Amer. Chem. Soc.*, 1965, **87**, 209; b, Sodium phthalocyanine tetrasulphonate, L. D. Rollman and R. T. Iwamoto, *J. Amer. Chem. Soc.*, 1968, **90**, 1455; c, Vitamin B_{12} (pH = 7), S. H. Cockle, H. A. O. Hill, J. M. Pratt, and R. J. P. Williams, *Biochem. Biophys. Acta*, 1969, **177**, 686; d, $Co(PhNC)_4Cl_2$; e, $Co(PhNC)_4Br_2$; f, $Co(PhNC)_4I_2$, J. P. Maher, *Chem. Comm.*, 1967, 632; J. P. Maher, *J. Chem. Soc.* (*A*), 1968, 2918; N. Kataoka and H. Kon, *J. Phys. Chem.*, 1969, **73**, 803; g, $Co(CN)_4Cl_2^{4-}$ (unpublished result). *h*–*h′* Various five and six-co-ordinate complexes (ref. 5)

Signs of the Metal Hyperfine Tensor Components.—Experience has shown that for normal d^7 Co^{II} complexes,[5] $A_{\parallel} > 0$ and $A_{\perp} < 0$. However, as $\Delta g_{\perp}$ increases, the results suggest (Figure 2) that $A_{\perp}$ changes sign in the region of $g_{\perp} \approx 2{\cdot}2$. [The result for the complex $Co(CN)_4Cl_2^{4-}$ (*g*), included in Figure 2, is new.] We conclude that $A_{\perp}$ is positive for values of $g_{\perp} \geqslant$ *ca.* 2·2. In particular, $A_{\perp}$ for $Co(CN)_4Cl_2^{4-}$ is taken to be positive.

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[10] G. Emschwiller, *C.R. Acad. Sci.* (*Paris*), 1959, **248**, 959.

[11] A. O. Caride, J. Danon, and S. I. Zanette, *J. Chem. Phys.*, **1970**, **52**, 4911.

[12] P. T. Manoharan and M. T. Rogers, 'E.s.r. of Metal Complexes,' ed. Teh Fu Yen, 1969, 143 (Hilger Ltd., London).

[13] R. Peterson and T. Vänngård, *Arkiv. Kemi*, 1960, **17**, 249.

This is strongly supported by the fact that after allowing for orbital magnetic contributions the calculated 2B value is quite unreasonable if $A_\perp$ is taken to be negative but is in good accord with expectation if it is taken to be positive.

Analysis of Data for $Ru(CN)_4Cl_2{}^{5-}$.—We can now consider the results for the analogous $M(CN)_4Cl_2{}^{n-}$ complexes where M = rhodium ($n = 4$) and ruthenium ($n = 5$). Comparing the results for the ruthenium complex with those for the corresponding rhodium complex[14] we can estimate an expected experimental value for $A_\perp$(Ru) using the value of $A_\perp$(Rh) = $-39{\cdot}5$ G, and the relative values $A_{iso}{}^\circ$(Rh) = -285 G and $A_{iso}{}^\circ$(Rh) = $-421{\cdot}3$ G, calculated from the best available wavefunctions.[15] Thus $A_\perp$ (expected) = $-39{\cdot}5 \times (-421{\cdot}3)/(-285) = -58$ G. The experimental value of *ca.* ± 60 G is in good agreement with this and we conclude that the correct value is $A_\perp$(Ru) = -60 G.

TABLE 2

Summary of e.s.r. data for the di-chlorinated complexes

	g-Tensor		Metal hyperfine tensor				Halogen hyperfine tensor	
Complex	$g_\parallel$	$g_\perp$	$A_\parallel$/G	$A_\perp$/G	2B°(M)	% d	$A_\parallel$/G	$A_\perp$/G
$Fe(CN)_4Cl_2{}^{5-}$	~2·002	2·197					*a*	4·7
$Co(CN)_4Cl_2{}^{4-}$	~2·002	2·287	+135	+63	+152·3	46	13	5
$Rh(CN)_4Cl_2{}^{5-}$	1·995	2·297	−43·6	−39·5	22·7	~22	29·7	13·3
$Ru(CN)_4Cl_2{}^{4-}$	~2·002	2·266	*a*	−60·5	−27·5 (^{99}Ru) −30·8 (^{101}Ru)	~21	17·5	8·5

[a] Unresolved.

The experimental results for the ruthenium and rhodium dichlorinated complexes can be compared with those for the corresponding iron and cobalt complexes (Table 2). The hyperfine coupling to chlorine almost doubles on going from the $3d$ to the $4d$ complexes, thus suggesting a considerable increase in delocalisation. Using the sign combinations discussed above, and remembering that g_N(Rh) and g_N(Rn) < 0 whereas g_N(Co) > 0, the approximate orbital populations can be calculated from the ruthenium and rhodium metal hyperfine tensors, by using the normal procedures[5] and the atomic values[15] listed in Table 2. In the calculation of s-orbital occupancy the value for $4d$ spin polarisation is calculated using the standard method.[16] Our results suggest that there is a marked fall in d-orbital population for the unpaired electron on going from $3d$ to $4d$ complexes. This arises at least in part from the greater delocalisation onto the ligands, and in part from an increase in the outer s-orbital contribution for the $4d$ elements. The isotropic metal hyperfine coupling stems from two opposing processes, spin polarisation giving a negative contribution, and population of the outer s-orbital, giving a positive contribution. The results show qualitatively that the outer s-orbital contribution is considerably greater for the $4d$ complexes.

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[14] R. P. A. Muniz, N. V. Vugman, and J. Danon, *J. Chem. Phys.*, 1971, **54**, 1284.

[15] Calculated from the wavefunctions of C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

[16] B. Goodman and J. B. Raynor, *Adv. Inorg. Radiochem.*, 1971, **13**, 135.