Unstable Intermediates. Part 166.[1] Cadmium and Mercury Centres in Irradiated Potassium Tetrathiocyanato-cadmate(II) and -mercurate(II)

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After exposure to ^{60}Co γ-rays at 77 K, the e.s.r. spectrum for $K_2[Hg(SCN)_4]$ shows well resolved, nearly isotropic, high-field lines assigned to magnetic centres containing ^{199}Hg and ^{201}Hg, with $A(^{199}Hg)$ = 8 900 G and g = 1.97. A triplet splitting of *ca.* 6 G on these features and on the central component is assigned to hyperfine coupling to one ^{14}N nucleus. This has been confirmed by measurements at *Q*-band frequencies. In dilute methanolic solution, an isotropic centre having $A(^{199}Hg)$ = 7 820 G is transformed into an anisotropic centre with $A_{\parallel}(^{199}Hg)$ = 7 691 G and $A_{\perp}(^{199}Hg)$ = 7 555 G on annealing. These results are interpreted in terms of the capture of electrons by $[Hg(SCN)_4]^{2-}$ ions in methanol to give $[Hg(SCN)_4]^{3-}$ having *ca.* 60% spin density in the 6*s* mercury orbital and 40% on the ligands. On annealing this becomes distorted, possibly by N-protonation, or loss of one ligand. For the pure solid it is suggested that the electron remains relatively mobile at 77 K until it is trapped at a defect in which one of the ligands is co-ordinated *via* nitrogen. Similar, but less well defined, results have been obtained for $K_2[Cd(SCN)_4]$ and its solutions in methanol.

It is now well established that ions such as Ag^+, Cd^{2+}, and Hg^{2+} with a full *d* shell readily add an extra electron to give atoms or ions with a $d^{10}s^1$ configuration. These are clearly identifiable by the detection of hyperfine coupling to magnetic nuclei in the e.s.r. spectra.[2-5] Aqueous or alcoholic solutions containing the parent cations give centres for which population of the outer *s* orbital is close to unity. However, covalent species have also been detected such as $[AgH]^+$ (ref. 3) and $[HgEt]^{2+}$ (ref. 6) for which the spin density on the metal is greatly reduced. The aim of the present work was to study complexes having ligands of intermediate covalency in the hope of obtaining some measure of the extent and mode of delocalization of the extra electron. When the work was well underway, an important paper by Isoya and Fujiwara[7] appeared in which the effect of high-energy radiation on potassium tetracyano-zincate(II), -cadmate(II), and -mercurate(II) is described. This work is closely related to our own and is outlined and discussed below.

Also, Eachus and Herring[8] have studied a mercury(I) centre formed from Hg^{II} doped into cadmium acetate and found an anisotropic hyperfine coupling to ^{199}Hg (and ^{201}Hg) with an isotropic component considerably reduced from the value for aquated Hg^I.

EXPERIMENTAL

Dipotassium tetrathiocyanatomercurate(II) of the highest commercial grade was not further purified, since it was established that recrystallization did not modify the results. The $K_2[Cd(SCN)_4]$ was prepared by adding a stoicheiometric amount of K[SCN] to $Cd[NO_3]_2$ in methanol and precipitating the desired salt with isopropanol. The white solid was washed to apparent dryness with cold methanol, isopropanol, and anhydrous diethyl ether.

Finely powdered salts were irradiated at 77 K in a Vickrad ^{60}Co source at a dose rate of 1.7 Mrad h^{-1} for up to 2 h. Dilute solutions in CD_3OD were irradiated at 77 K as small spherical beads. E.s.r. spectra were measured on a Varian E3 spectrometer at 77 K. Samples were annealed in the insert Dewar flask after decanting the liquid nitrogen, and were recooled to 77 K whenever the continuously monitored spectra showed significant changes.

RESULTS AND DISCUSSION

In each case, intense features were obtained in the central (*g* 2) region. These included the central lines from the mercury(I) and cadmium(I) centres of interest, but no attempt was made to interpret the remaining poorly defined features.

Potassium Tetrathiocyanatomercurate(II).—This gave well defined high-field features assigned to centres containing ^{199}Hg and ^{201}Hg [Figure 1(a)]. These appear to be almost isotropic triplets [Figure 1(b)] which closely resemble a central triplet assigned to the centres containing non-magnetic mercury isotopes [Figure 1(c)]. On annealing, these resonances were lost together, without any significant changes. The high-field features are the expected $|F = 1, m_F = 0\rangle \rightleftharpoons |F = 1, m_F = -1\rangle$ transition for ^{199}Hg and the $|F = 2, m_F = -2\rangle \rightleftharpoons |F = 2, m_F = -1\rangle$ transition for ^{201}Hg, where $F = I + S$. As usual, none of the other transitions was detectable. [^{199}Hg has $I = \frac{1}{2}$, $\mu_N = 0.4979$ nuclear magnetons, and is 16.86% abundant; ^{201}Hg has $I = \frac{3}{2}$, $\mu_N = -0.5513$ nuclear magnetons, and is 13.24% abundant.] The isotropic hyperfine coupling constants (Table 1) were derived from these features using the full Breit–Rabi equation.[9,10]

This centre was not formed from solutions of $K_2[Hg(SCN)_4]$ in methanol (CD_3OD). Instead, two centres, A and B (Figure 2) were formed, A being quantitatively transformed into B on slight annealing above 77 K. The derived parameters are given in Table 1, those for centre B being obtained by the method outlined previously.[11]

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[1] Part 165, R. J. Booth, S. A. Fieldhouse, H. C. Starkie, and M. C. R.Symons, *J.C.S. Dalton*, 1976, 1506.

[2] L. Shields, *Trans. Faraday Soc.*, 1966, **62**, 1.

[3] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1329, 1336.

[4] R. S. Eachus and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 3080.

[5] M. C. R. Symons and J. K. Yandell, *J. Chem. Soc.* (*A*), 1971, 760.

[6] B. W. Fullam and M. C. R. Symons, *J.C.S. Dalton*, 1974, 1086.

[7] J-I. Isoya and S. Fujiwara, *Bull. Chem. Soc. Japan*, 1972, **45**, 2182.

[8] R. S. Eachus and F. G. Herring, *Canad. J. Chem.*, 1971, **49**, 562, 2868.

[9] G. Breit and I. Rabi, *Phys. Rev.*, 1931, **38**, 2082.

[10] J. F. Nafe and E. B. Nelson, *Phys. Rev.*, 1948, **73**, 718.

[11] R. J. Booth, H. C. Starkie, M. C. R. Symons, and R. S. Eachus, *J.C.S. Dalton*, 1973, 2233.

Similar experiments were made with $K_2[Cd(SCN)_4]$ and its solutions in methanol. High-field features from ^{111}Cd and ^{113}Cd were detected but they were far broader than the corresponding mercury features and we were unable to tell whether or not there was any contribution from ^{14}N. However, the estimated 5*s* character for the species formed in the pure salt (Table 2) was about the same as that for the mercury centre. In the remaining discussion, attention is focused on the better defined mercury centres. In view of the isotropic nature of the significant spectra in the two salts, single-crystal studies would have given no further information and were not attempted.

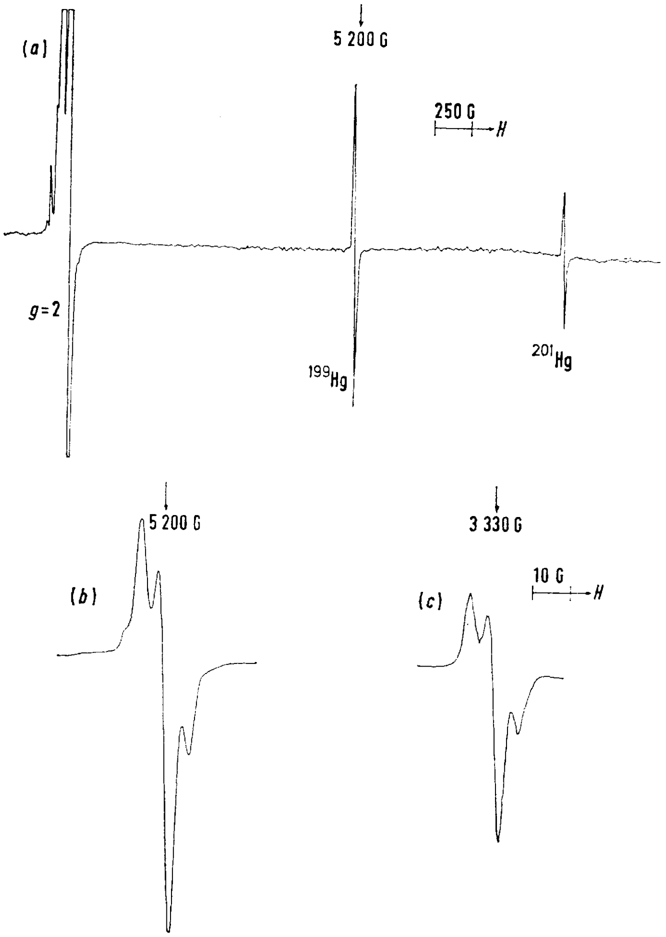


FIGURE 1 First-derivative *X*-band e.s.r. spectra for $K_2[Hg(SCN)_4]$ after exposure to ^{60}C γ-rays at 77 K showing (*a*) central and high-field features assigned to a mercury(I) centre, (*b*) the high-field ^{199}Hg feature, and (*c*) the central triplet

We offer the following explanation for these results. The isolated anions in methanol glasses act as good electron traps, as evidenced by the almost complete absence of e_t^- centres after irradiation. Thus we suggest that centre A is $[Hg(SCN)_4]^{3-}$, with the unpaired electron in a symmetrical σ^* orbital comprising *ca.* 69% 6*s* character on mercury, the remaining spin density being largely on the ligands. [This is based on the experimen-

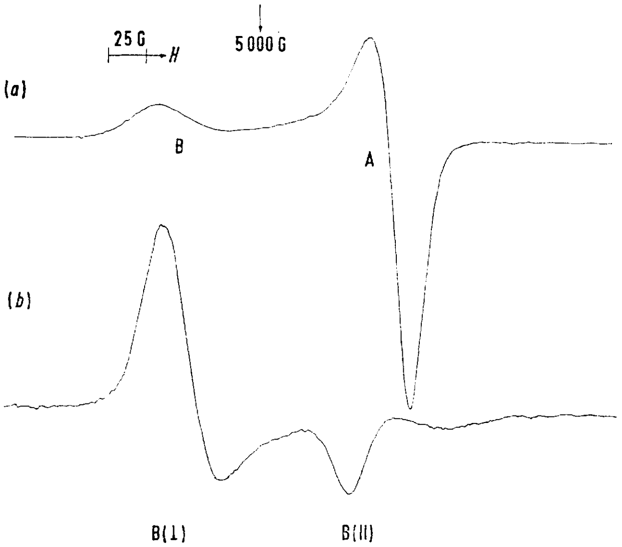


FIGURE 2 First-derivative *X*-band e.s.r. spectra for $K_2[Hg(SCN)_4]$ in CD_3OD after exposure to ^{60}Co γ-rays at 77 K showing the high-field ^{199}Hg feature for a mercury(I) centre (A) and (B), and (*b*) the ^{199}Hg feature for centre (B) after slight annealing

TABLE 1

E.s.r. data for magnetic centres formed from $[Cd(SCN)]_4^{2-}$ and $[Hg(SCN)_4]^{2-}$ and from $[Zn(CN)_4]^{2-}$, $[Cd(CN)_4]^{2-}$, and $[Hg(CN)_4]^{2-}$

		Metal hyperfine coupling [a]					
Host	Radical	$A_\parallel$	$A_\perp$	A_{iso}	$g_\parallel$	$g_\perp$	$g_{av.}$
$K_2[Cd(SCN)_4]$	$[Cd(SCN)_4]^{3-}$ [b]			3 208			1.997
$K_2[Hg(SCN)_4]$	$[Hg(SCN)_4]^{3-}$ [c]			8 946			1.997
$K_2[Hg(SCN)_4]$–CD_3OD	A $[Hg(SCN)_4]^{3-}$			7 800			1.98
	B	7 691	7 555	7 600			2.00
$K_2[Zn(CN)_4]$ [d]	$[Zn(CN)_4]^{3-}$ or $[Zn(CN)_3]^{2-}$	131	110	117 (^{67}Zn)	2.000	1.999	
$K_2[Cd(CN)_4]$ [d]	$[Cd(CN)_4]^{3-}$ or $[Cd(CN)_3]^{2-}$	1 580	1 470	1 506 (^{113}Cd)	1.990	1.998	
$K_2[Hg(CN)_4]$ [d]	$[Hg(CN)_4]^{3-}$ or $[Hg(CN)_3]^{2-}$	5 020	(4 580, 4 560)	4 720 (^{199}Hg)	1.97	1.96	

[a] Calculated using the full Breit–Rabi equation. [b] Thought to be $[Cd(NCS)(SCN)_3]^{3-}$. [c] Thought to be $[Hg(NCS)(SCN)_3]^{3-}$; $A(^{14}N) \approx 6$ G. [d] Ref. 7.

tal result for Hg^+ in acidic glasses of *ca.* 13 000 G.[5]] † The lack of anisotropy implies that no major distortion has occurred, but the relatively low mercury hyperfine coupling shows that there is significant covalency forcing the antibonding electron on to sulphur. The small negative *g* shift nevertheless implies some occupancy of the outer $6p$ manifold.

However, on annealing, a small anisotropy is introduced, corresponding to partial occupancy of one of the $6p$ orbitals (p_z). It is difficult to estimate the orbital population because of the many errors involved, but comparison with the values for unit occupancy calculated from the wavefunctions of Froese [12] suggests a value of *ca.* 0.2. Thus the loss of $6s$ character (*ca.* 0.02) is less than the gain in p character. We suggest that this distortion has been induced by some chemical change, rather than being spontaneous. This is because, in our experience, spontaneous distortions usually occur directly at the time of electron addition unless powerful steric opposing forces are operating. In view of the high negative charge, the distortion could be caused by protonation of one of the ligand nitrogen atoms. Alternatively, it could be caused by complete loss of one thiocyanato-ligand.

The anion $[Hg(SCN)_4]^{3-}$ does not form in the pure salt at 77 K, presumably because electron transfer remains relatively facile in the absence of distortion. We therefore suggest that such mobile electrons are preferentially trapped at centres that fortuitously already have a built-in distortion. The detection of one unique ligand having a relatively strongly interacting ^{14}N nucleus leads to the suggestion that there is a small equilibrium number of $[Hg(NCS)(SCN)_3]^{2-}$ anions present in the crystalline material, and that these have a slightly greater electron affinity than the $[Hg(SCN)_4]^{2-}$ anions, possibly because of the weaker σ bonding between mercury and nitrogen.

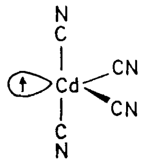
The $2s$ population on nitrogen of *ca.* 0.011 is relatively low, and the degree of anisotropy cannot be greater than *ca.* 2 G, corresponding to a $2p$ population $\leqslant 0.06$. Thus the extra electron, whilst probably favouring the Hg–NCS σ^* orbital, is strongly localized on the metal, as expected for a more ionic bond. This is supported by the fact that the $6s$ population is actually greater than that for the centre thought to be $[Hg(SCN)_4]^{3-}$. Thus the N-thiocyanato-ligand has the effect of constraining the extra electron on to mercury.

Comparison with the $[Hg(CN)_4]^{3-}$ *Centre.*—Reference has already been made to the $[Zn(CN)_4]^{3-}$, $[Cd(CN)_4]^{3-}$, and $[Hg(CN)_4]^{3-}$ centres reported by Isoya and Fujiwara.[7] These workers obtained well defined powder spectra showing narrow features for complexes containing ^{47}Zn, ^{111}Cd, ^{113}Cd, ^{199}Hg, and ^{201}Hg isotopes. These showed very marked anisotropy and so single-crystal studies were also undertaken. We had independently observed the powder spectra for the cadmium and mercury centres. The results, summarized in Table 1, show a markedly reduced isotropic coupling and a relatively large anisotropic coupling. The isotropic coupling constants for ^{113}Cd and ^{111}Cd can be converted into approximate spin densities using the experimental values for $^{113}Cd^+$ and $^{111}Cd^+$,[13] giving a $5s$ population of *ca.* 0.24 and 0.28 for the two major species detected. We have used the wavefunctions of Froese [12] to obtain a rough estimate of the $5p_z$ character and find a value of *ca.* 0.75 for these centres. In the light of the results for the mercury centre (Table 2), we think this is an overestimate, but it does confirm the suggestion that the orbital involved is an $s + p$ hybrid on cadmium. These results closely resemble those for covalent molecules such as those of tin.[14,15] Two possibilities are (*a*) a distortion towards a trigonal bipyramid, with the electron constrained in a largely non-bonding orbital, (I), and (*b*) loss of one cyanide to give (II). In other words, the covalent ligands exert a strong control on the mixing of *s* and *p* orbitals, and tend to exclude the unpaired electron from the σ-bonding region.

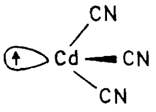
TABLE 2

Approximate orbital populations for the centres in Table 1

Radical	Metal a_s^2	Metal $a_{p_z}^2$
$[Hg(SCN)_4]^{3-}$ (A)	0.60	
(B)	0.58	*ca.* 0.2
$[Hg(NCS)(SCN)_3]^{3-}$	0.69	
$[Cd(NCS)(SCN)_3]^{3-}$	*ca.* 0.70	
$[Zn(CN)_4]^{3-}$ or $[Zn(CN)_3]^{2-}$	0.25	*ca.* 0.60
$[Cd(CN)_4]^{3-}$	0.28	*ca.* 0.75
or $[Cd(CN)_3]^{2-}$	0.24	0.75
$[Hg(CN)_4]^{3-}$ or $[Hg(CN)_3]^{2-}$	0.36	*ca.* 0.5



(I)



(II)

The same considerations apply to the zinc and mercury complexes (Table 2). [It was originally stated [7] that the spin density on zinc was far lower than that on cadmium, but this does not seem to be the case: our calculations suggest that all three centres are comparable.]

The results are in marked contrast with ours for the thiocyanato-complexes, which display either no asymmetry or an asymmetry that is small compared with those for the cyano-complexes. It is this contrast that leads us to the view that one ligand has been lost in the case of the cyanides. In the particular case of centre B in methanol, a situation somewhere between these

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† 1 G = 10^{-4} T.

[12] C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

[13] P. H. Kasai, *Phys. Rev. Letters*, 1968, **21**, 67.

[14] J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1972, **15**, 322.

[15] S. A. Fieldhouse, A. R. Lyons, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 1966.

extremes is found. If one ligand has been lost in this instance, then the covalent effect constraining the unpaired electron into the non-bonding orbital ($\sim sp^3$) must be less powerful for $[Hg(CNS)_3]^{2-}$ than for $[Hg(CN)_3]^{2-}$. We conclude that the tetracyano-complexes behave in a similar manner to many tetrahedral covalent molecules, whilst the tetrathiocyanato-complexes behave more like ionic complexes, although there is considerable delocalization on to the ligands.

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