Electron Spin Resonance Spectra of Cd^+, Hg^+, and Tl^{2+}

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Summary The cations Cd^+, Hg^+, and Tl^{2+}, formed by γ-irradiation of rigid solutions containing Cd^{2+}, Hg^{2+}, and Tl^{3+}, respectively, have been identified by their e.s.r. spectra.

THE radical cations Cd^+, Hg^+, and Tl^{2+} are frequently invoked as intermediates in the radiolysis and photolysis of solutions of various salts of these elements, but e.s.r. evidence for their formation in corresponding rigid solutions is almost non-existent.[1] For Cd and Hg, this is because the normal isotopes ^{112}Cd and ^{114}Cd, and ^{200}Hg are non-magnetic, and hence the e.s.r. powder spectra of the corresponding cations are broad single lines which cannot be used for purposes of identification. Both elements have magnetic isotopes in fair abundance, but satellite lines have not been reported in previous studies of this type.[1]

We suggest a reason for this deficiency and present data which, on the one hand, firmly establish the formation of these ions in the radiolysis of solutions of their parent salts, and on the other provide information which will enable diagnostic tests to be made for their presence.

Previous failure to detect the hyperfine components for Cd^+, Hg^+, and Tl^{2+} arose because the hyperfine coupling constants are so large that the low-field components are undetectable at the normal operating frequency (9GHz), whilst the high-field components occur at higher fields than are normally scanned in e.s.r. experiments (Table). This is because the unpaired electrons are in *s*-atomic orbitals, and the nuclear magnetic moments are unusually large.

For Cd^+ and Hg^+, the magnetic parameters can be readily derived from the experimental spectra, despite the absence of low-field lines, because the strong central line gives the *g*-tensor directly. However, the usual approximate form of the Breit–Rabi equation is not satisfactory and the full equation[2] has been used to derive the hyperfine coupling constants included in the Table. The constants calculated for ^{199}Hg from the result for ^{201}Hg, although close to the experimental value for ^{199}Hg, lie outside experimental error. This is, we feel, an effect of the large quadrupole moment of ^{201}Hg.

TABLE

Magnetic parameters for Hg^+, Tl^{2+}, and Cd^+

Ion	Isotope	Solvent	Approximate field position for frequency of 9·2 GHz. (G)	g-Tensor	Experimental hyperfine tensor[a] (G)	Ref.
Hg^+	^{200}Hg	7M-$HClO_4$	3310	1·997 ± 0·002		
	^{199}Hg	,,	5470		12,500 ± 100	(11,200 ± 150)[d]
	^{201}Hg	,,	7350		4540 ± 50	
	^{200}Hg	EtOH	3310	1·987 ± 0·01		
	^{199}Hg	,,	5410		11,490 ± 300	(9,980 ± 250)[d]
	^{201}Hg	,,	7070		4040 ± 100	
Tl^{2+}	^{203}Tl	7M-$HClO_4$	6180[b], 7210[c]	1·997 ± 0·002	43,260 ± 500	
	^{205}Tl					
	^{203}Tl	ZnS			25,266 ± 10	
		crystal		2·0095 ± 0·0005	25,524 ± 10	3a
	^{205}Tl	KCl				
	^{203}Tl	crystal		2·010 ± 0·002	37,610 ± 30[b]	3b
	^{205}Tl					
Cd^+	^{112}Cd			$g_\parallel = 2·001$		
		H_2SO_4	3288[b]	$g_\perp = 1·994$		
	^{114}Cd			$g_{av} = 1·996$		
	^{111}Cd	,,	4466[b]		3680 ± 130	
	^{113}Cd					
	^{112}Cd	EtOH		$g_\parallel = 1·9924$		
	^{114}Cd		3328[b]	$g_\perp = 1·9896$		
				$g_{av} = 1·9905$		
	^{111}Cd	,,	4416		3280 ± 130	
	^{113}Cd					
	^{111}Cd	Argon		$g_{iso} = 2·0006$	5137 ± 1	4
	^{113}Cd				5374 ± 1	

[a] Calculated using full Breit-Rabi equation. [b] Separate components not resolved. [c] N.m.r. transition. [d] Calculated for ^{199}Hg from the ^{201}Hg result.

Since there is no diamagnetic thallium nucleus, the results for Tl^{2+} would be impossible to analyse completely, were it not for the fact that an extra transition between the two upper hyperfine energy levels appears ($|F = 1, M_F = 0> \longleftrightarrow |F = 1, M_F = +1>$), which is not normally detected in e.s.r. experiments. The field value of this line, together with that of the normal high field transition

$$(|F = 1, M_F = -1 > \longleftrightarrow |F = 1, M_F = 0 >)$$

enabled us to calculate the hyperfine coupling constant and g-tensor given in the Table.[3]

For all these ions, the distinctive feature of one or two lines at very high-field values is a strong diagnostic test for the presence of these ions, and there are sufficient differences in the spectra of the ions to differentiate unambiguously between them.

Our results for Cd^+ ions can be compared with the recent data of Kasai[4] for this ion in an argon matrix (Table). The reduction of 40% in our value of the hyperfine coupling constant is very marked, and stems, we believe, from the fact that our ions were produced by reduction of solvated Cd^{2+} ions, whilst Kasai's were obtained by oxidation of matrix-isolated cadmium atoms.

Since the medium is rigid, and the positive charge is not completely lost, we postulate that the residual solvation of Cd^+ by water is considerable, and hence the energy of the 5s-orbital is effectively raised by admixture with the ligand orbitals. The orbital scheme put forward to explain the results for the Ag^0 formed in alkali halide crystals from Ag^+ ions is appropriate here also.[5]

We have also detected dimeric radicals such as Cd_2^{3+} which is isoelectronic with Ag_2^+ [6] and mixed dimers such as $(CdAg)^{2+}$. Results for these species will be reported in detail soon.

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