Electron Spin Resonance Studies of Electron-trapping by Cations in Some Silver and Cadmium Salts

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Summary A species closely resembling the cation Cd^+ has been detected in γ-irradiated $CdCO_3$ at 77K, and identified as $(CdCO_3)^-$, with about 80% of the spin-density on Cd; other cadmium and silver salts gave species with cation spin-densities ranging from 2 to 80%.

ALTHOUGH electron- and hole-trapping by polyatomic anions in pure salts is well established,[1,2] we know of no examples of electron-trapping at monatomic cations. The former is effective because the anions change shape when the electrons are captured, but the latter would normally be considered to be impossible in terms of simple band theory for ionic crystals. However, we have detected satellite lines from ^{111}Cd and ^{113}Cd in γ-irradiated $CdCO_3$ at 77K which show that the spin-density on single cadmium ions is at least 80%, by comparison with the value for Cd^+ in an argon matrix.[3] (See Table).

We postulate that the species is best represented as the molecular entity $(CdCO_3)^-$, in which there is an effective σ-bond, possibly between cadmium and carbon. In order to check this possibility, we have studied a range of comparable salts, with the results listed in the Table.

Magnetic parameters and derived spin-densities for metal centres in various γ-irradiated salts and related systems

Salt	Magnetic centre	A_{iso} (Metal)G	Spin-density (%) on metal[a]	anion
$AgNO_3$	$(Ag\cdots NO_3)^-$	14·9	2	*ca.* 100[b]
$Cd(NO_3)_2$	$(Cd\cdots NO_3)$	*ca.* 300	*ca.* 3	*ca.* 100
Ag_2CO_3	$(Ag\ldots CO_3\cdots Ag)^-$	53[c]	$\geqslant$15(2Ag)	$\leqslant$ 85
$CdCO_3$	$(Cd\cdots CO_3)^-$	(4230)[d] (4470)	83	17
$CdCO_3 + Hg^{2+}$	$(Hg\cdot\cdot CO_3)^-$	13,100	*ca.*85	*ca.* 15
$Cd(HCO_2)_2$	$(Cd\cdots CO_2)$	*ca.* 530	*ca.*10	*ca.* 90
Ag^+ in H_2O glass	$(Ag\cdots H)$	103·6[c]	$\geqslant$14	55

[a] Based on the isotopic coupling, by comparison with the atomic value (Ag), the results of Kasai,[3] or from our values for the species in aqueous and alcoholic glasses (Hg^+). R. S. Eachus, M. C. R. Symons, and J. K. Yandell, *Chem. Comm.*, 1969, 979.
[b] W. C. Mosley and W. G. Moulton, *J. Chem. Phys.*, 1965, **43**, 1207.
[c] Considerable anisotropic coupling giving *p*- or *d*-character.
[d] ^{111}Cd and ^{113}Cd. The ratio is correct for these isotopes.

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The nitrates gave metal coupling constants that are normal for ion-pairs, and the ^{14}N hyperfine tensors confirm that the species are best described as NO_3^{2-}. Silver carbonate gave a radical containing two equivalent silver ions, giving a total spin-density of 15% on silver. [This species has been reported previously, but was, in our view, erroneously described as NO_2.[4]] The species AgH^+[5] is an example in which almost equal sharing occurs. The species $(CdCO_2)^+$, formed in γ-irradiated cadmium formate is included since CO_2^- is a common radiation product in carbonates. A comparable species is not formed in $CdCO_3$.

The cation Hg^+ was also detected in some samples of $CdCO_3$, which contained Hg^{2+} impurity. It remains possible that the "Cd^+" species is trapped either close to a vacancy or to some non-interacting impurity which serves to make the particular Cd^{2+} ions favourable electron-trapping centres. However, the species is well defined, and is readily lost on warming. We hope to obtain more definitive results by studying single $CdCO_3$ crystals.

The results given in the table form a consistent series in terms of the relative electron affinities of the cations and ionisation potentials of the radical anions.

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[3] P. H. Kasai, *Phys. Rev. Letters*, 1968, **21**, 67.
[4] N. A. Ashford and G. A. Noble, *J. Chem. Phys.*, 1968, **49**, 4720.
[5] R. S. Eachus and M. C. R. Symons, *Chem. Comm.*, 1969, 285.