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PART 4.—THE EFFECT OF COMPLEXING ON THE ULTRA-VIOLET SPECTRUM OF IODIDE IONS

BY T. R. GRIFFITHS * AND M. C. R. SYMONS † Chemistry Dept., The University, Southampton

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The ultra-violet spectra of iodide complexes of zinc, cadmium and mercury of the general type MI^+ , MI_2 , MI_3^- and MI_4^{2-} are recorded, and the nature of the electronic transitions discussed. A wide range of solvents was used, and their effect on the spectra of MI_2 , which for zinc and cadmium differ markedly from the spectra of the molecules in the gas phase, is considered in detail. The results are compared with those for simple, solvated iodide ions, and for iodide ions in "contact" ion-pairs in which there is no covalent bonding between iodide and the cation.

In previous papers we have considered the problem of interaction between iodide ions and solvent molecules,¹⁻³ and between iodide ions and cations such as tetra-alkyl ammonium ions, to which covalent bonding is impossible.⁴ In particular, the changes which occur in the ultra-violet spectrum of iodide with changes in solvation,¹⁻³ and on formation of "contact" ion-pairs,⁴ have been studied and the following interpretation advanced. The first excited state of solvated iodide ions is, in part, defined by the first layer of solvent molecules surrounding the ion, and transitions to this state are described as charge transfer to solvent (C.T.T.S.). When iodide is in contact with a cation, but not bonded to it, the electronic transition involves movement of one of the 5 p electrons of iodide to an outer orbital of the cation, the simplest example being the first transition of alkali-metal iodides in the gas phase.

There is often uncertainty regarding the structure of units generally described as "ion-pairs" and detected particularly by conductance methods. In formulating theories to explain the results of such studies, it would be an advantage to know the structure and concentration of one or more of the units embraced by this terminology. One of the aims of this, and of an earlier study,⁴ is to stress that spectrophotometry is often a useful method for detecting and estimating the concentrations of "contact" ion-pairs ⁴ and complex ions or molecules in which there is a real contribution from covalent bonding between cation and anion. Our studies have been confined to interactions between cations and iodide ions. "Contact" ion-pair formation has been discussed elsewhere.⁴ Here we are concerned with complex formation. In different contexts, this problem has already been considered by others.⁵⁻⁷

The choice of metal ions for this study was governed by our desire to differentiate between transitions involving outer electrons largely on iodide and those involving electrons largely localized on the metal ion. This, and the fact that the spectra of neutral di-iodides in the gas phase are all known, led us to select zinc, cadmium and mercuric iodides for detailed investigation. The cations have a closed shell configuration, $(s)^2$, $(p)^6$, $(d)^{10}$ in the ground state, and the first excited states of the free ions are sufficiently far removed not to contribute directly to the near ultra-violet spectra under consideration. Thus, we are able to examine the

^{*} present address : North-East Essex Technical College, Colchester.

[†] present address : Chemistry Department, The University, Leicester.

nature of electronic transitions of iodide bonded to these ions, and hence compare these spectra with those of solvated iodide ions.

Despite these simplifications, one difficulty remains, namely, that various different species could contribute to the measured spectra. For example, cadmium iodide could give, in solution, the ions CdI^+ , CdI_3^- and CdI_4^{2-} in addition to free cadmium and iodide ions and the neutral molecules. Another complication is that solvent may be bonded to the cation in any, or all, of these complexes. These factors are discussed in the light of the results, together with the nature of the electronic transitions. No attempt has been made to determine thermodynamic constants for the systems studied.

| Table | 1.—Details | OF THE | UL | FRA-VIOLET | SPECT | RA OF | IODIDE | COMPLEXES | OF | ZINC, |
|-------|------------|--------|-----|-------------------|-------|-------|---------|-----------|----|-------|
| | CA | DMIUM | AND | MERCURY | TAKEN | FROM | THE LIT | ERATURE | | |

| solvent | | added salt λ_{max} (m μ) | | €max | ref. | |
|---------|-------------------------|---------------------------------------|------------|---------------------------|------|--|
| ZnI_2 | H ₂ O (dil.) | | 226·2, 193 | 14,000 | С | |
| ,, | H_2O (conc.) | — | 238·5 | 5,000-14,000 ^b | 16 | |
| " | H_2O | KI a | 238 | 16,000-36,000 b | 16 | |
| ,, | EtOH | _ | 217, 189 | 6,500 | 17 | |
| | | | 216 | 6,500 | 18 | |
| CdI_2 | H_2O (dil.) | _ | 226·2, 193 | 14,000 | С | |
| ,, | H_2O (conc.) | | 250 | 10,000 | 16 | |
| •• | H ₂ O | KI a | 258 | 35,000 | 16 | |
| ,, | MeOH | | 239 | 7,000 | 20 | |
| •• | EtOH | | 238, 192 | 6,500 | 17 | |
| | | | 243 | 6,500 | 18 | |
| •• | n-PrOH | | 240-2 | 9,000 | 18 | |
| | MeCN | | 240-2 | 9,000 | 18 | |
| HgI_2 | H_2O (dil.) | | 265 | 4,600 | 19 | |
| ,, | H_2O | KI | 323-4, 267 | 23,000 | 19 | |
| ,, | MeOH | | 267 | 2,200 | 20 | |
| | EtOH | _ | 270, 213 | 2,200 | 17 | |
| | | | 274, 213 | 2,200 | 18 | |
| ,, | EtOH | NaI a | 329, 273 | 19,000 | 19 | |
| ,, | t-BuOH | | 275 | | 21 | |
| •• | CHCl ₃ | _ | 275 | | 21 | |
| ,, | CCl ₄ | | 275 | | 21 | |

a excess, b depending upon concentration, c spectrum of aqueous iodide ion.

Various features of the ultra-violet spectra of halide complexes of zinc, cadmium and mercury recorded by others are summarized in table 1. A large amount of work involving other techniques has been devoted to these complexes, particularly in aqueous solution. Reviews of these studies are given in ref. (8)-(15). Here, it is recalled that there is no general agreement regarding the formulae and structure of these complexes and, partially because of this, stability constants for specified complexes have been reported which differ by factors up to 10⁴.

MATERIALS

EXPERIMENTAL

All water used was purified by double distillation from alkaline permanganate under oxygen-free nitrogen. Other solvents were B.D.H. "special for spectroscopy" or Eastman Kodak Co. "Spectrograde" and were dried, when necessary, by distillation from calcium sulphate or hydride.

Tetra-n-butylammonium iodide, purified by recrystallizing several times from acetone, and drying *in vacuo* had m.p. 146.5° (lit. 145°). Tetra-n-butylammonium perchlorate, prepared from the iodide and silver perchlorate in acetone, and recrystallized from n-butanol, had m.p. $207-8^{\circ}$ (lit. $203-4^{\circ}$).

Zinc and cadmium perchlorates, prepared from 72 % perchloric acid and the corresponding oxide, were dehydrated by heating *in vacuo*. Cadmium perchlorate was not

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freed from water completely since it decomposed if heated strongly. Mercuric perchlorate cannot be prepared anhydrous without decomposition and the formation of basic salts. Solutions of mercuric oxide in perchloric acid tended to complex formation, detected by optical absorption bands in spectral regions where none were expected. It is hoped to report this phenomenon more fully later. However, mercuric iodide in 72 % perchloric acid gave a new band at 245 m μ , which may well be due to HgI⁺, which, by analogy with ZnI⁺ and CdI⁺, should have a band in this region. We therefore have tentatively included this value in table 3. Other solutes were A.R. grade and were used without further purification.

SPECTROPHOTOMETRY

Spectra were measured using a Unicam S.P. 500 spectrophotometer fitted with a S.Z.G. 500 photomultiplier, or a Unicam S.P. 700 recording spectrophotometer. Concentrations and cell sizes were selected such that total optical densities ranged between 0.1 and 1.0, and the cells were thermostatted by use of a Unicam S.P. 570 cell-housing.

RESULTS

Significant features of results for the pure salts are summarized in table 2, and some typical spectra are shown in the figures. The temperature dependence

TABLE 2.—DETAILS OF THE ULTRA-VIOLET SPECTRA OF IODIDE COMPLEXES OF ZINC, CADMIUM AND MERCURY IN VARIOUS SOLVENTS

| | solvent | added salt | $\lambda_{max}(m\mu)$ | [€] max d | E_{\max}/dT (cal/deg) |
|------------------|---------------------------------|------------------------|-----------------------|--------------------|-------------------------|
| \mathbf{ZnI}_2 | iso-PrOH | _ | 218.3 | 10,000 | 22.6 |
| ,, | iso-PrOH | $Zn(ClO_4)_2 a$ | 209.2 | 6,000 | |
| ,, | n-BuOH | | 217.1 | 9,000 | 16→22 |
| ,, | n-BuOH | $Zn(ClO_4)_2 a$ | 210.2 | 5,400 | |
| ,, | MeCN | | 217.1 | 7,500 | 15 |
| ,, | MeCN | $Zn(ClO_4)_2 a$ | 211.8 | 6,000 | |
| ,, | Me_2CO | | 218 | _ | _ |
| CdI ₂ | iso-PrOH | | 241.9 | 6,600 | $-3 \rightarrow +3$ |
| ,, | iso-PrOH | $Cd(ClO_4)_2 a$ | 227.9 | 5,200 | · _ |
| ,, | iso-PrOH | KI a | 248-50 | | |
| ,, | n-BuOH | | 243.1 | 7,400 | 14 |
| ,, | n-BuOH | $Cd(ClO_4)_2 a$ | 225.6 | 5,000 | |
| ** | n-BuOH | KI a | 248-50 | | _ |
| ,, | MeCN | | 243.1 | 6,500 | 7 |
| ,, | MeCN | $Cd(ClO_4)_2 a$ | 225.1 | 5,000 | _ |
| HgI ₂ | H ₂ O | _ | 265, 210 | | 0 |
| ,, | MeCN | _ | 265 | 3,000 | 0 |
| ,, | MeCN | (n-Bu) ₄ NI | 260·5, ca. 301 | | |
| ,, | MeOCH | | 264 | 3,000 | 0 |
| | 0 | | | | |
| ,, | MeOCH | (n-Bu) ₄ NI | 259, ca. 303 | | |
| | Ö | | - | | |
| " | EtOCMe | | 269 | 3,000 | • 0 |
| | | | | | |
| | EtOCMe | (n-Bu)/NI | 261 ca. 306 | | |
| " | | (11 200)41 (1 | 201, cu. 500 | | |
| | CH2Ch | | 272 | 3.000 | 0 |
| ,, | CH ₂ Cl ₂ | $(n-Bu_{4})NI$ | 261, ca, 306 | | _ |
| ,, | iso-octane | | 275 | | |
| " | D.M.F. b | | 273, 301 | | |
| " | D.M.F. b | (n-Bu)₄NI | 305→335 ¢ | | |
| ,, | a excess. | b N.N-dimethylfo | rmamide. | ¢ see fig. 4 at | nd 5. |

of E_{max} , the energy corresponding to maximum absorption, is also given in table 2 since this parameter was found to be important when discussing the spectrum of iodide in various solvents.^{1,3}

Results obtained from solutions containing a large excess of the corresponding perchlorates are also given in table 2. The effect of varying the temperature was not studied systematically but was relatively small in selected cases.



FIG. 1.—Low-energy ultra-violet absorption bands of zinc, cadmium and mercuric iodides.
(1) ZnI₂ in iso-PrOH; (2) CdI₂ in iso-PrOH; (3) HgI₂ in CH₂Cl₂.





(1) $ZnI_2 + Zn(ClO_4)_2$ in iso-PrOH; (2) $CdI_2 + Cd(ClO_4)_2$ in iso-PrOH.

Since solvated iodide ions absorb strongly in the 220-240 m μ region the effect of adding an excess of potassium iodide could not be observed with zinc iodide. Equivalent amounts were not sufficient to give appreciable quantities of new complexes. For cadmium iodide in n-butanol and in isopropanol containing excess potassium iodide, clear evidence for a new band at 248 m μ was obtained (fig. 3). In contrast with zinc and cadmium iodides, equivalent amounts of iodide

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produced marked changes in the spectra of mercuric iodide and the appearance of isobestic points (fig. 5) show that successive equilibria leading to HgI_3^- and $HgI_4^2^-$ are simple and occur consecutively.



FIG. 3.—Ultra-violet absorption of cadmium iodide in n-butanol in the presence of excess potassium iodide.

(1) Using n-BuOH as reference; (2) using n-BuOH containing the appropriate [KI] as reference.



FIG. 4.—Spectra of solutions of mercuric iodide in N,N-dimethylformamide. (1) alone; (2), (3) and (4) together with increasing concentrations of $(n-Bu)_4NI$.

DISCUSSION

DETECTION OF IODIDE IN A COMPLEX

It has been suggested that the characteristic and large changes in the band maxima of iodide with change in environment can be used to distinguish between purely solvated iodide ions, and iodide either in contact with, or covalently bonded to, cations.⁴ From the results now reported, a clear distinction between solvated iodide and iodide associated with zinc, cadmium or mercuric cations can be



FIG. 5.—Spectra of solutions of mercuric iodide in N,N-dimethylformamide containing excess tetra-n-butylammonium iodide.

(1) as (4) in fig. 4; (2)-(5) further increase in $(n-Bu)_4NI$.

made. For example, zinc iodide in isopropanol has a band at 218 m μ which is very close to that for free iodide in this solvent.¹ However, potassium iodide in methyl cyanide has a peak at 246 m μ ,¹ whereas the band for zinc iodide in methyl cyanide remains in the 218 m μ region. Simple "contact" ion-pairs such as those described earlier ⁴ were found to be unimportant constituents in the solvents used, so we conclude that the new species formed are best described as complexes with some covalent bonding between iodide and the cation.

In the following, we consider in turn the number of iodide ions bonded to each cation, the possibility of solvent co-ordination, the structure of the complexes, and the nature of the electronic transitions which give rise to the observed spectra.

ANION-CATION RATIOS

The assignment given in table 3 is based in part on the conclusions of others ¹⁵⁻²¹ but largely upon reasoning of the type now outlined for cadmium iodides. In

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many non-aqueous solvents cadmium iodide has a low-energy band in the 242 m μ region. This is probably due to CdI₂ molecules but, in view of the difference between these spectra and that of the molecule in the gas-phase, the possibility that the absorbing species is formed from CdI₂ by a disproportionation such as

$$2CdI_2 \rightleftharpoons CdI^+ + CdI_3^-$$

cannot be ignored.

Table 3.—Average values for the maxima of the low-energy transitions of various iodide complexes (in $m\mu$)

| | MI+ | MI_2 | $MI_{\overline{3}}$ | MI42- |
|---------|-------|----------|---------------------|-------|
| zinc | 210 | 218 | | 238 |
| cadmium | 226.5 | 243 | 249 | 258 |
| mercury | 245 | 268, 210 | 305, 263 | 335 |

However, addition of excess cadmium perchlorate results in the loss of the band at 242 m μ and the appearance of a new band at 226 m μ together with isobestic points at 233 m μ , and 218 m μ . Excess iodide gives a band at 248 m μ in non-aqueous solvents and at 258 m μ in water. Since Raman studies establish that the major complex in the latter solution is CdI₄²⁻, the other bands must be assigned as in table 3. Allocation of the bands for zinc and mercuric iodides is based on similar reasoning.

When the concentration of aqueous zinc or cadmium iodides is less than 10^{-2} M, only the band for aqueous iodide is observed. On the other hand, mercuric iodide, which in contrast with the other two is sparingly soluble in water, dissolved almost entirely as the neutral molecule (see table 1). In other solvents, however, there is clear evidence for the disproportionation

$2HgI_2 \rightleftharpoons HgI^+ + HgI_3^-$.

This is especially marked for dimethylformamide, the band at $304 \text{ m}\mu$ (HgI₃) being well resolved.

STRUCTURE

There is abundant evidence that the tetra-iodide complexes are regular tetrahedra with no solvent molecules co-ordinated to the central metal. However, the possibility of solvent co-ordination arises for all the other complexes.

It is convenient to consider the dihalide molecules first, since the spectra and structure of these linear molecules in the gas-phase are known. Some pertinent details are listed in table 4. Detailed studies of Raman spectra for solutions of the dihalides in n-butanol and acetone have shown that zinc, cadmium and mercuric iodides each give rise to one strong line at 165, 142 and 150 cm⁻¹ respectively.⁸

TABLE 4.—Relevant properties of the gaseous iodides of zinc, cadmium and mercury

| | λ_{\max} (m μ) | Raman frequencies (cm ⁻¹) ³² | bond lengths(Á) 33 |
|---------|-----------------------------|---|--------------------|
| ZnI_2 | 238 30 | | 2.42 ± 0.02 |
| CdI_2 | 261, 220 ²⁹ | _ | 2.58 ± 0.02 |
| HgI_2 | 266, 224 31 | 155 (v ₁) | 2.58 ± 0.03 |

The band for mercuric iodide is very close to that for the molecule in the gas phase, and it is concluded that the molecules are linear and unionized in these solvents.

In our attempts to interpret the ultra-violet spectra of zinc and cadmium iodides one reasonable postulate was that in solution, two solvent molecules were co-ordinated to the metal, giving a tetrahedral unit similar to that found for the tetrahalides. These molecules would then have C_{2v} symmetry and one would expect to find, for the MI₂ part of the complex, three Raman lines (two polarized) instead of a single line.²² Thus, the results of Delwaulle and co-workers ⁸ strongly suggest that these molecules are linear in solution.

Proof of linearity does not establish that solvent is not co-ordinated: for example, four solvent molecules might bond in a plane to give octahedral co-ordination. However, the Raman studies show no sign of any lines due to metal-solvent bonds, and the values for v_1 for the dihalides in a wide range of solvents of very different co-ordinating powers remain remarkably constant.⁸ Thus, if solvent is oriented in this sense, the bonding must be relatively weak and non-specific. This possibility is considered further in the next section.

Because of the stability associated with linear co-ordination,²³ it is very probable that HgI⁺ has one solvent molecule quite strongly bonded to mercury. The same may be true of CdI⁺ and ZnI⁺. Little can be said of the tri-iodo complexes, which could be planar, or tetrahedral with one solvent quite strongly bonded to the central metal atom. Evidence from Raman studies is not conclusive.⁸

NATURE OF THE ELECTRONIC TRANSITIONS IN MI_2

When discussing the spectra of alkali-metal halide ion-pairs in the gas phase, or of contact ion-pairs in solution, it is found that the results are well accommodated in terms of a transition of an outer *p*-electron of the halide ion into the outer *s*-atomic orbital of the cation. Hence one finds, in general, two bands separated by an energy increment close to the difference in energy between the ${}^{2}P_{\frac{1}{2}}$ and ${}^{2}P_{\frac{1}{2}}$ states of the halogen atom. Katzin has listed a large number of molecules and ions containing halogen for which, in many cases, such doublets are observed.²¹ He has suggested that halogen atoms are formed in the excited states of all these compounds.²¹ For the particular compounds considered in our study, we wish to re-examine and modify this point of view.

Considering the linear molecule MI₂, a transition to give an iodine atom in the excited state would have to be written MI₂ \rightarrow MI+I: this representation is not in accord with a variety of observations, including the following: (i) fine structure is resolved in the second band for HgI₂ in the gas phase, (ii) the band separations are not very close to the theoretical splitting required, (iii) the second band is far more intense than the first, and (iv) if covalent bonding is at all important, one would expect the transition to involve $p-\pi$ non-bonding electrons on iodine rather than the more tightly held $p-\sigma$ electrons, in which case it is hard to see how an iodine atom could be formed *during* the act of light absorption.

It seems more probable that the transition is of the type discussed by Walsh for B—A—B molecules with 16 valence-electrons.²⁴ In the gas phase the molecules are certainly linear,²⁵ with a ${}^{1}\Sigma_{g}^{+}$ ground state. Walsh represents the first transition for HgI₂, which is a continuum, as the forbidden ${}^{1}\Delta_{u} \leftarrow {}^{1}\Sigma_{g}^{+}$, and the second, more intense band in the 210 m μ region, as ${}^{1}\Sigma_{u}^{+} \leftarrow {}^{1}\Sigma_{g}^{+}$.²⁴

Both these transitions involve the transfer of an iodine $p-\pi$ electron in the outer π_g orbital into an antibonding $\overline{\pi}_u$ orbital. To a fair approximation, the π_g level may be thought of as non-bonding on iodine, and the $\overline{\pi}_u$ orbital as non-bonding on the central atom. Thus, one could expect a steady shift of these bands to lower energies on passing from zinc to mercury. This trend is strong on going from zinc to cadmium but the bands for gaseous CdI₂ and HgI₂ have very similar energies. It is significant that the metal-iodine bond lengths for CdI₂ and HgI₂ are also very similar, being considerably greater than that for ZnI₂.³³

In solution, the two bands for HgI_2 are remarkably close to those for the molecule in the gas phase, but for CdI_2 and ZnI_2 there is a very marked shift to higher energies, even for such solvents as acetone or methyl cyanide.

This effect could be interpreted in a variety of ways, some of which can be dismissed on other grounds. For example, it is possible that two solvent molecules

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are co-ordinated to the metal ion, giving a tetrahedral unit. As was stressed in the previous section, evidence from Raman spectroscopy is strongly against this conclusion, but if, for some reason, the expected Raman pattern is obscured, this would provide a simple explanation for the changes in the ultra-violet spectra relative to the gas-phase results.

Alternatively, we could say that this is a general solvent effect such as that found by Kosower for transitions involving a marked change in dipole.²⁶ However, for the transitions described above, there is no net dipole moment in ground or excited states although there is a movement of negative change inwards. Thus, we could not expect a very marked effect, and in particular, we could look for a trend with change in solvent, similar to those found by Kosower.²⁶ This is not found for ZnI₂, or CdI₂.

The explanation that we favour is that, for ZnI_2 and CdI_2 but probably not for HgI₂, the metal ions are co-ordinated very weakly to four solvent molecules in addition to the two iodides, this giving an octahedral structure with the iodides in the trans-configuration. The presence of the weakly bonding σ -electrons of the solvent molecules would greatly destabilize the upper state for both the $1\Sigma_{u}^{+} \leftarrow 1\Sigma_{g}^{+}$ and $1\Delta_{u} \leftarrow 1\Sigma_{g}^{+}$ transitions described above, and hence a strong shift to the ultraviolet would be expected.

It is now necessary to ask why HgI₂ does not interact in a similar manner. We tentatively suggest that the difference lies in the electronic structure of this molecule. Jørgensen ²⁷ and Orgel ²³ have pointed out that the d^{9s} state is far closer to the d^{10} ground state for Hg²⁺ than for Zn²⁺ or Cd²⁺. Orgel shows that hybridization of the d_z^2 and s orbitals give two new levels, one of which can "accept" the ligands, giving two strong, short bonds. The electrons thus removed from the bonding region will tend to concentrate in the plane normal to the molecular axis, and hence will repel any solvent molecules in this region. Similarly, the n- π transition will be made more difficult by the presence of these electrons, both in the gas phase and in solution. In this way, the short Hg—I bonds, the proximity of the transitions for gaseous HgI₂ to those of CdI₂, and the lack of solvent effect for HgI₂, are all rationalized.

SPECTRA OF OTHER COMPLEXES

In general, the same sort of reasoning is thought to apply to the other complexes considered. MI^+ cations probably have at least one solvent molecule fairly strongly bonded to the metal. Perchlorates were used because this ion has a very small tendency to co-ordinate in this way, but we cannot rule out completely the possibility that the perchlorate ion is involved in some instances.

It is noteworthy that for each metal, the energy of maximum absorption for the low-energy band decreases regularly as the number of co-ordinated iodide ions increases from one to four. In a general sense one might say that individual $p-\pi$ electrons on iodide become more non-bonding in nature as their number increases and hence less energy is required for electron transfer. However, changes in co-ordination must alter the nature of the excited state in a complex manner, so this conclusion cannot be extended to other compounds. The spectrum tentatively assigned to HgI⁺ can be compared with that of MeHgI, which has a band at 230 m μ quite comparable in intensity.²⁸ The similarity in these spectra suggests that one solvent molecule is strongly bonded to mercury in HgI⁺ giving a linear complex. The somewhat higher energy required for the transition in MeHgI can then be understood in terms of the increased electron releasing power of CH₃ relative to the co-ordinated solvent molecule.

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