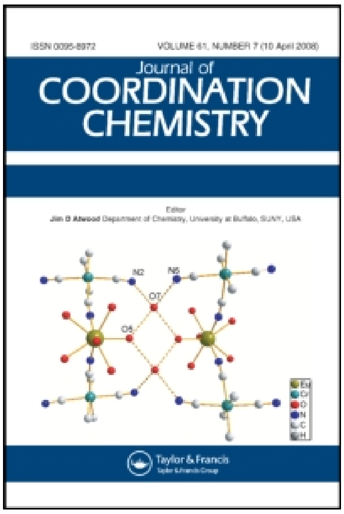

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Wagner-Czauderna, Elzbieta , Koczorowska, Anna and Kalinowski, Marek K.(1999) 'STABILITY OF 15-CROWN-5 AND BENZO-15-CROWN-5 COMPLEXES WITH ALKALI METAL CATIONS IN NONAQUEOUS MEDIA', Journal of Coordination Chemistry, 46: 3, 265 — 276

To link to this Article: DOI: 10.1080/00958979908048471

URL: http://dx.doi.org/10.1080/00958979908048471

J. Coord. Chem., 1999, Vol. 46, pp. 265–276
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STABILITY OF 15-CROWN-5 AND BENZO-15-CROWN-5 COMPLEXES WITH ALKALI METAL CATIONS IN NONAQUEOUS MEDIA

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(Received 23 September 1997)

The formation of alkali metal cation complexes with 15-crown-5 and benzo-15-crown-5 in ten organic solvents has been investigated by cyclic voltammetry at 25°C. Stability constants of the resulting 1 : 1 complexes have been determined by monitoring the shift in reduction potentials of the cations against ligand concentration. Based on the results obtained the dependences of stabilities of the complexes on Gutmann donicity of the solvents and on standard Gibbs transfer energies of the metal ion from water to a given solvent have been analyzed and discussed.

Keywords: 15-crown-5; benzo-15-crown-5; alkali metal; complexes; stability constants; solvent effects

INTRODUCTION

Selective binding of alkali metal cations (M^+) in solution is a distinctive feature of macrocyclic ligands. A good example, one of many, is provided by the coronands; their complexing power has been discussed in a plethora of papers.[1–6] The process of cation – macrocycle interaction depends on several factors related to characteristic properties of the reacting ion and ligand. First, the ratio of the radius of the cation and of the ligand cavity is important. Secondly, the nature and number of the donor atoms influence complex formation. The substitution of one or more oxygen atoms of

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crown ethers by sulfur or nitrogen atoms results in a decrease of complex stabilities with alkali metal cations.[7] The strikingly large difference between complexing properties of 18-crown-6 (18C6) and 18-crown-5 has recently been analyzed.[8] Solvation is also known to have a profound effect on the stability constants of macrocyclic complexes.[9–11] In fact, solvation phenomena of cations play a dominant role, but the influence of the solvent on complex formation is not restricted to them. The interactions of the ligand 18C6 with acetonitrile, nitromethane and dimethylsulfate have been studied in detail.[12–14] More recently, the interaction of 15-crown-5 (15C5) with nitromethane, acetonitrile and acetone has been reported; it was found that these can be associated non-selectively with the host 15C5.

Thus the solvent effect on the cation binding properties of coronands is of great importance. The literature[1–6] contains a great number of data on crown ether complexes in various media but only several attempts have been made to correlate the change of stability constants, K_s, with selected solvent parameters. Among them, the reciprocal of electric permittivity[16] and the Kirkwood function[17–19] were applied for binary mixtures of organic solvents with water[16,18,19] and for a series of pure alcohols.[17] The observed changes of K_s with these parameters were interpreted on the basis of a simple dielectric continuum model. However, such a formalism is not applicable to all electrolyte systems and fails in the prediction of most solvation phenomena. In other words, it is unlikely that this model can be applied to aprotic solvents.

In reality, the solvation parameters of cations may be related to the Lewis basicity of solvents, expressed *e.g.*, by DN, the Gutmann donor number.[20] Accordingly, selected crown ether complexes were reported to show inverse correlations of $\log K_s$ with DN.[21–26] Quite recently, however, Raevsky, Schneider and co-workers[27] have suggested to use the standard Gibbs transfer energies, ΔG_t^o, of the metal ion from water to a given solvent as the best parameter. Although this suggestion is fully justified from the formal point of view, the real situation seems to be more complicated. This qualification is important as regards comparing correlations of $\log K_s$ with ΔG_t^o and DN for 18C6-K^+ complexation (Table 3 in Ref. [27]). This problem, together with an analysis of the solvent effect on the complexation of alkali metal cations by 15C5 and benzo-15-crown-5 (B15C5) will be discussed in the present work.

The literature[1–6] contains a wealth of results on these complexes in several solvents. However, the data reported in a given medium differ, sometimes by more than one order of magnitude. By way of example, this is evident with the 15C5-Li^+ complex in acetonitrile for which extreme values of $\log K_s = 3.60$[28] and 5.34[29] were reported. Next, for the 15C5-K^+ system in the same solvent one can find the values of 2.98[28] and 4.33.[14] Taking into account the fact that such discrepancies are not exceptional, we have decided to remeasure (in some media to measure) the complexation equilibria under unequivocally defined conditions. The respective K_s values were determined by cyclic voltammetry in 10 organic solvents. The solvents, both protic and aprotic, were selected so as to give a respectable range of DN and ΔG_t^o values as conveniently possible.

EXPERIMENTAL

Crown ethers 15C5 and B15C5 from Merck were used without further purification. Reagent grade $LiClO_4$, $NaClO_4$, $KClO_4$ and $CsClO_4$ (all from Merck) were also used without purification except for drying over P_2O_5 at 120°C. Tetraethylammonium perchlorate (TEAP) was prepared from tetraethylammonium iodide (TEAI), which was recrystallized from ethyl acetate, and $HClO_4$ (all from Merck). The compound was purified by repeated recrystallization from triply distilled water and dried at 60°C *in vacuo*. Dimethylsulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), acetone (AC), acetonitrile (ACN), methanol (MeOH) and ethanol (EtOH) were purchased as Fluka certified chemicals for UV-spectroscopy and used without purification. All remaining solvents, propylene carbonate (PC), *N*,*N*-dimethylacetamide (DMA), formamide (FM) and tetramethylene sulfone (TMS), all from Merck, were dried and purified by procedures described in the literature.[30]

Cyclic voltammetric measurements were carried out with a static mercury electrode model 303A (PAR) in a three-electrode arrangement. The counter-electrode was a platinum wire; an AgCl/Ag couple in 0.1 M aqueous tetraethylammonium chloride served as a reference electrode. This last was separated from the electrolyzed solution by means of a vycor disk. All the solutions were deaerated with pure argon and an inert atmosphere was maintained in the electrochemical vessel during the experiment. A PAR 273A potentiostat was used for the measurements. It was controlled by an IBM PC AT computer by means of the software (M270) from PAR. Experiments were performed at 25 ± 0.5°C (in TMS at 30 ± 1°C).

RESULTS AND DISCUSSION

Before we proceed with the interpretation of our results, several questions need to be answered. The first of these is related to the reversibility of electrochemical processes. The experiments performed by cyclic voltammetry in solutions containing 0.4 mM $MClO_4$ and 0.1 M TEAP indicate that reversible or nearly reversible one electron transfers are observed in all the solvents under investigation. The cathodic currents are in either case controlled by diffusion, in full agreement with the results reported in earlier papers.[23,32] Thus, the $(E_{pa} - E_{pc})/2$ values may be assumed as approximately equal to the formal potentials, E°, for the redox systems in (1).

$$M^{+}_{solv} + e \rightleftharpoons M(Hg) \tag{1}$$

Secondly, the addition of 15C5 and B15C5, respectively, shifts the E° values in a negative direction, while the reversibility of the electrode process is preserved as before. Thus the variation of the potential may be related to the ligand concentration (c_{crown}) and the stability constant by the well-known Lingane equation

$$\Delta E = E' - E^{o} = (RT/F)\ln(K_s\, c_{crown}) + (RT/F)\ln(i_{crown-M^+}/i_{M^+}) \tag{2}$$

where E' stands for the potential determined at a given c_{crown} value, whereas the ratio of limiting currents $i_{crown\,-\,M^+}/i_{M^+}$ corresponds to a change in the diffusion coefficient of M^+ upon complexation. Recall that equation (2) was derived assuming that only the 1 : 1 complex is formed in solution, and c_{crown} is much larger than the concentration of M^+ cation. As follows from our experiments, the ΔE values are linearly related to $\log c_{crown}$ and $\Delta\Delta E/\Delta\log c_{crown}$ were found to be $60 \pm 5\,mV/\log c_{crown}$ units in all the media under study; therefore only 1 : 1 complexes were indeed identified. The concentration range of the ligand added was about 4–50 mM.

Next, the problem of ion-pair formation in $M^{+} \ldots ClO_4^-$ systems should be clarified. Since dilute solutions of the alkali metal perchlorates were used, it was unlikely that complex formation had significant competition from ion association. In reality, the salts are unassociated in PC,[32] DMF,[33] DMSO,[34] DMA[35] and, probably, in FM[36] solutions. Next, the analysis of conductance data indicates that alkali metal perchlorates are rather weakly associated in ACN,[36] TMS[37] and MeOH.[37] Only in acetone really incomplete dissociation is expected because the ion-pair formation constants are 1680, 641, 307 and 223 for $LiClO_4$, $NaClO_4$, $KClO_4$ and $CsClO_4$, respectively.[38] However, as follows from the work of Buschmann *et al.*,[39] even in that medium the ion-pair formation effect may not be taken into account. According to the performed simulation, the abovementioned authors have pointed out that "if the values of the stability constant and of the ion-pair formation constant differ at least by the one order of magnitude the existence of ion pairs does not influence the value of the calculated stability constant. Even in the case that both values are of the same order of magnitude the value of the stability constant is not influenced very much".[39] Thus, taking into account the above statement, we have calculated respective K_s values by ignoring the ion association of the salts in all media. The resulting data are collected in Table I.

One can observe that the K_s values for B15C5 complexes are smaller in comparison with those for 15C5. Such behaviour may be easily explained. Due to the electron withdrawing effect of the benzo group of B15C5 the donor properties of the neighbouring donor atoms are reduced. Also, it should be pointed out that some of the stability constants already published agree well with those values. This is evident for the 15C5-Li^+ complex in AC,[39] PC[40,41] and MeOH,[21,42] for 15C5-Na^+ in ACN,[28,40] PC,[40] AC[39] and DMF,[43] for 15C5-K^+ in ACN[17,44] and AC[39] and finally for 15C5-Cs^+ in ACN,[14,29] AC,[39] PC[40] and FM.[45] The agreement is also observed for the B15C5-Li^+ complex in ACN,[46] for B15C5-Na^+ in ACN,[14] PC,[48] DMF[43] and DMSO,[43] for B15C5-K^+ in ACN[14] as well as for B15C5-Cs^+ in ACN[14] and MeOH.[46] Complexation of Na^+ and K^+ ions by 15C5 and B15C5 in MeOH solutions was studied by many authors[4-6] and most of the stability constants reported agree with respective values presented in Table I.

Having determined the K_s values, we are able to analyse the solvent effect on the complexation equilibria. Since energetics of cation desolvation play a decisive part in determining these quantities, we have performed a series of

TABLE I Logarithms of formation constants for the complexes of crown ethers with alkali metal cations in various solvents at 25°C (0.1 M TEAP as electrolyte)

Ligand	*Cation*	$\log K_s$									
		ACN	*TMS*[a]	*PC*	*AC*	*FM*	*DMF*	*DMA*	*DMSO*	*MeOH*	*EtOH*[b]
15C5	Li^+	4.2	4.3	4.1	3.5	1.3	1.0	< 1	< 1	1.2	1.7
	Na^+	4.9	4.7	4.8	4.3	2.4	2.0	1.7	1.2	3.3	3.7
	K^+	4.4	4.3	3.9	4.2	2.1	2.0	1.5	1.2	3.4	3.9
	Cs^+	3.2	3.5	3.3	3.5	1.5	1.0	< 1	< 1	2.6	2.9
B15C5	Li^+	3.8	3.7	3.7	3.2	1.0	< 1	< 1	< 1	1.1	1.5
	Na^+	4.5	4.4	4.4	3.7	2.0	1.5	1.3	1.2	3.0	3.5
	K^+	4.2	4.0	3.8	3.7	1.8	1.4	1.2	1.1	3.2	3.7
	Cs^+	3.4	3.2	3.0	3.1	1.3	1.0	< 1	< 1	2.1	2.5

[a] At 30°C. [b] Owing to sparing solubility of TEAP, 0.1 M TEAI was used as electrolyte.

least-squares regression calculations according to the general equation

$$\log K_s = \alpha P + \beta \tag{3}$$

where P marks the solvent parameter, and α and β stand for regression coefficients. In our analysis DN and ΔG_t^o values were chosen as prime parameters. It is apparent that complexation increases in strength with a decrease in the donor number of the solvent. We have started, therefore, with correlations of $\log K_s$ against DN, and Table II shows the essential results of the computations. As can be seen, all the correlations are statistically significant, but the most serious deviations are with alcohols as solvents. If the points for MeOH and EtOH are excluded, the correlations are generally improved. Recall, however, that methanol and ethanol are rather distinctive solvents and glaring discrepancies exist between their DN and DN_{bulk} values.[20,47] The values of 19 and 20 for MeOH and EtOH,[20] respectively, served to establish corresponding straight lines; the respective values of DN_{bulk} (25.7 and 31.4) do not conform to the correlations. Note also that $DN = 24.7$ was used for formamide.

The α and β coefficients of equation (3) in which $P = DN$ have defined physical meaning. The first of these may be treated as a sensitivity factor of $\log K_s$ to change of the electron-donating solvent properties whereas the second determines the stability constant of a given complex in the medium characterized by $DN = 0$. This is particularly noteworthy as it suggests that in such a solvent and, probably, in the gas phase, stability sequences for the complexes of alkali metal cations with both 15C5 and B15C5 should be as follows $Li^+ \sim Na^+ > K^+ > Cs^+$. Obviously, this order is surprisingly different from those observed under a number of experimental conditions (Table I). It should be stressed therefore that an *ab initio* quantum mechanical study clearly showed[48] that the binding affinity of 18C6 decreases with increasing alkali metal cation size. This suggests that gas-phase 18C6 will most strongly bind Li^+ rather than K^+ which is of perfect size to occupy the cavity of the coronand. Therefore the results of Glendening *et al.*[48] are in accordance with the stability sequence predicted for the complexes of 15C5 and B15C5.

Next, the α values for the complexes formed by both ligands change linearly with $1/r_c$, where r_c is the cation radius on the Ladd scale.[49] In our opinion this finding proves that the desolvation of cations upon complexation is extremely important to the energetics of the process. A more precise discussion of such dependences is presented in a previous report.[50]

TABLE II Parameters of the correlation equation $\log K_s = \alpha DN + \beta$

No.	*Complex*	α^a	β^a	n^b	r^c	F^d	*Solvents*
1	15C5-Li$^+$	-0.283 ± 0.147	8.02 ± 2.86	8	0.887	22.1	ACN, TMS, PC, AC, FM, DMF, MeOH, EtOH
2		-0.275 ± 0.030	8.21 ± 0.58	6	0.991	641.9	ACN, TMS, PC, AC, FM, DMF
3		-0.257 ± 0.208	7.37 ± 4.25	6	0.864	11.8	PC, AC, FM, DMF, MeOH, EtOH
4	15C5-Na$^+$	-0.235 ± 0.024	8.25 ± 0.52	10	0.992	519.6	ACN, TMS, PC, AC, FM, DMF, DMA, DMSO, MeOH, EtOH
5		-0.237 ± 0.009	8.29 ± 0.18	8	0.999	5069.7	ACN, TMS, PC, AC, FM, DMF, DMA, DMSO
6		-0.234 ± 0.036	8.17 ± 0.58	9	0.992	439.9	ACN, TMS, PC, FM, DMF, DMA, DMSO, MeOH, EtOH
7	15C5-K$^+$	-0.207 ± 0.040	7.42 ± 0.85	10	0.974	146.4	The same set of solvents as in 4
8		-0.205 ± 0.032	7.31 ± 0.68	8	0.989	262.7	The same set of solvents as in 5
9	15C5-Cs$^+$	-0.193 ± 0.063	6.33 ± 1.33	8	0.950	55.1	The same set of solvents as in 1
10		-0.196 ± 0.073	6.34 ± 1.40	6	0.966	56.7	The same set of solvents as in 2
11	B15C5-Li$^+$	-0.313 ± 0.175	8.17 ± 3.18	7	0.899	21.1	ACN, TMS, PC, AC, FM, MeOH, EtOH
12		-0.271 ± 0.032	7.73 ± 0.16	5	0.998	725.2	ACN, TMS, PC, AC, FM
13		-0.295 ± 0.282	7.70 ± 5.36	5	0.887	11.0	PC, AC, FM, MeOH, EtOH
14	B15C5-Na$^+$	-0.226 ± 0.030	7.67 ± 0.65	10	0.986	304.1	The same set of solvents as in 4
15		-0.227 ± 0.023	7.70 ± 0.49	8	0.995	620.4	The same set of solvents as in 5
16		-0.228 ± 0.033	7.72 ± 0.73	9	0.987	268.4	The same set of solvents as in 6
17	B15C5-K$^+$	-0.212 ± 0.038	7.23 ± 0.84	10	0.976	159.0	The same set of solvents as in 4
18		-0.209 ± 0.021	7.08 ± 0.48	8	0.995	553.1	The same set of solvents as in 5
19	B15C5-Cs$^+$	-0.189 ± 0.044	6.03 ± 0.83	8	0.974	111.0	The same set of solvents as in 1
20		-0.191 ± 0.038	6.07 ± 0.75	6	0.990	188.5	The same set of solvents as in 2

[a] 95% confidence intervals are given. [b] Number of experimental points. [c] Correlation coefficient of linear regression. [d] Fisher's statistical test.

It is well known that standard Gibbs transfer energies, ΔG_t^o, have been successfully applied to correlate a large number of seemingly unrelated data in solution chemistry.[51,52] Following the suggestion made previously[27] we also tried to correlate the $\log K_s$ values for the 15C5 and B15C5 complexes with ΔG_t^o. The regression parameters calculated according to equation (3) in which $P = \Delta G_t^o$ are thus shown in Table III.

In computing regressions presented in Table III, we have applied the ΔG_t^o values tabulated by Marcus.[51] Since appropriate quantities for Li^+ in AC and TMS as well as for Na^+ in AC are not available in this monograph, we have not considered further lithium complexes in acetone and tetramethylene sulfone and sodium complexes in acetone solutions. Remembering this fact, several problems arise when one tries to compare the data presented in Tables II and III. First, the correlations of $\log K_s$ against ΔG_t^o are considerably less meaningful in comparison with those obtained with DN as an explaining parameter; extremely poor relationships ($r \sim 0.3$) exist for the Cs^+ complexes of 15C5 and B15C5. Secondly, for sodium and potassium complexes with both ligands, very serious deviations are seen with TMS as solvent. If these values are excluded, the correlations of $\log K_s$ *vs* ΔG_t^o are considerably improved.

Gibbs transfer energies of single ions derive from a variety of extrathermodynamic assumptions employing different experimental techniques and reference solvents. Thus, there is a considerable scatter in the published data; the values for a given ion and a given solvent can vary by as much as over a dozen or so $\mathrm{kJ\,mol^{-1}}$ and TMS should be treated as one of these examples.[52] It can, therefore be safely concluded, in spite of limited evidence, that the solvent donor number is a better descriptor of the medium effect on complexation equilibria than the Gibbs energy of transfer.

Finally, we would like to analyse shortly the results presented in Table III of an earlier report.[27] Investigating the medium effect on the complexation equilibria of the 18C6-K^+ system, the authors pointed out that the best explaining solvent parameter is ΔG_t^o. For the set of 7 solvents, namely ACN, PC, AC, DMF, DMSO, MeOH and hexamethylphosphoric triamide (HMPT) they have found a relationship in the following form

$$\log K_s = (0.115 \pm 0.039)\Delta G_t^o + (5.13 \pm 0.40) \qquad (4)$$

which holds with $r = 0.960$ and $F = 58.3$ (95% confidence intervals are presented). The result was compared with the correlation of $\log K_s$ against

TABLE III Parameters of the correlation equation $\log K_s = \alpha \Delta G_t^\circ + \beta$ (see footnotes to Table II)

Complex	α	β	*n*	*r*	*F*	*Solvents*[a]
15C5-Li$^+$	0.086 ± 0.058	1.61 ± 0.92	6	0.890	17.0	The same set of solvents as in 3
15C5-Na$^+$	0.097 ± 0.059	3.13 ± 0.68	9	0.827	15.2	The same set of solvents as in 6
	0.103 ± 0.031	2.89 ± 0.49	8	0.956	63.7	ACN, PC, FM, DMF, DMA, DMSO, MeOH, EtOH
15C5-K$^+$	0.097 ± 0.062	3.09 ± 0.60	10	0.787	13.0	The same set of solvents as in 7
	0.105 ± 0.046	2.91 ± 0.47	9	0.896	28.4	ACN, PC, AC, FM, DMF, DMA, DMSO, MeOH, EtOH
15C5-Cs$^+$	0.033 ± 0.092	2.69 ± 0.84	8	0.337	0.8	The same set of solvents as in 9
B15C5-Li$^+$	0.088 ± 0.076	1.27 ± 1.29	5	0.904	13.9	ACN, PC, DMF, MeOH, EtOH
B15C5-Na$^+$	0.096 ± 0.059	2.81 ± 0.66	9	0.833	15.9	The same set of solvents as in 6
	0.108 ± 0.025	2.56 ± 0.40	8	0.970	96.7	ACN, PC, FM, DMF, DMA, DMSO, MeOH, EtOH
B15C5-K$^+$	0.102 ± 0.061	2.81 ± 0.58	10	0.808	15.1	The same set of solvents as in 7
	0.110 ± 0.044	2.63 ± 0.44	9	0.913	35.2	ACN, PC, AC, FM, DMF, DMA, DMSO, MeOH, EtOH
B15C5-Cs$^+$	0.026 ± 0.090	2.45 ± 0.81	8	0.279	0.5	The same set of solvents as in 19

[a] For numbers see correlations presented in Table II.

DN for which the following equation was proposed

$$\log K_s = (-0.156 \pm 0.076)\mathrm{DN} + (8.32 \pm 1.96) \qquad (5)$$

$(r = 0.897,\ F = 24.8)$. Comparing the corresponding values of r and F the latter correlation was found to be poorer than the former.[27] We assume, however, that this supposition is rather illusory.

The problem follows from the fact that both correlation equations were computed for different sets of solvents; analyzing regression (5) the authors[27] included additionally water. In this situation recalculation of equation (4) for 8 solvents (ACN, PC, AC, DMF, DMSO, HMPT, MeOH and water) seemed to be required. Therefore, we have performed such recalculation and, consequently, taking into account the fact that for water $\Delta G_t^o = 0$, expression (6) can be written,

$$\log K_s = (0.108 \pm 0.115)\Delta G_t^o + (4.73 \pm 1.10) \qquad (6)$$

for which $r = 0.685$ and $F = 5.3$. It should be emphasized that regression (5) must be compared with (6) and not with (4).

An additional problem should be mentioned. In expression (5) water is represented by its $\mathrm{DN}_{bulk} = 33$. This value was estimated from the regression of DN *versus* δ^{23}Na (NMR spectra) uncorrected for magnetic susceptibility;[53] the corrected value is about 38. If we use the latter value, correlation (5) is visibly improved as

$$\log K_s = (-0.150 \pm 0.054)\mathrm{DN} + (8.27 \pm 1.35) \qquad (7)$$

with $r = 0.939$, $F = 45.0$.

Thus it may be thought that DN is a poorer descriptor of the medium effect than ΔG_t^o as was suggested?[27] The answer is rather not. Although both these parameters are colinear to some extent, application of DN seems to be more successful in the description of solvent influence on the complexation of alkali metal cations by coronands. This conclusion is particularly valid for non-proton donating liquids for which appropriate donor numbers are unequivocally defined.

Acknowledgments

This paper was sponsored by the State Committee for Scientific Research, through grant 3 T09A 089 09.

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