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Transition Metal Complees of Diethanolamine and N-methyldiethanolamine

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The preparation of the following complexes of diethanolamine (deaH) and N-methyldiethanolamine (medea) is described: $[Ni(deaH)_2]X_2 . H_2O$ ($X = Cl, Br$); $[Ni(deaH)_2]Br_2$; $[Ni(deaH)_2]Cl_2 . 2H_2O$; $[Cu(deaH)_2](NO_3)_2$; $[M(deaH)H_2O]X$, ($M = Ni$, $X = Cl, Br$; $M = Co$, $X = Cl, Br, NO_3$); $[Ni(deaH)(dea)]X . H_2O$, ($X = Br, I$), $[Co(deaH)(dea)]Br$; $[Ni(deaH)_2(dea)]X . H_2O$, ($X = NO_3, I$); $[M(medea)_2]X_2$, ($M = Co, Ni$, $X = Cl, Br, I, NO_3$); *and* $[Co(medea)_3](NO_3)_2$.

Electronic spectra, infrared spectra and magnetic moments are reported and discussed in terms of suggested structures for the complexes.

Introduction

In this paper we report a study of complexes of diethanolamine (deaH, $NH(CH_2CH_2OH)_2$) and N-methyldiethanolamine (medea) with cobalt(II), nickel(II) and copper(II) salts. Complexes of diethanolamine have been reported by Heiber.[1] We have repeated some of his preparations and have also prepared a number of new complexes. There have been a number of publications dealing with complexes of diethanolamine in solution,[2-5] particularly with copper(II). E.S.R. evidence has been presented[2] for the formation of a dimeric 1:1 complex with copper(II), while pH studies have shown[4] the presence of a range of 1:2 complexes in solution including those with singly and doubly deprotonated ligand, in which the oxygen proton is lost. We have studied the complexes of N-methyldiethanolamine for comparison purposes. These have not been reported previously.

Experimental Section

The 2:1 complexes of N-methyldiethanolamine were readily precipitated on adding the ligand to ethanolic solutions of the appropriate hydrated metal salt in 2:1 molar ratios. Acetone was used for the preparation of $[Ni(medea)_2]I_2$. Addition of ligand to metal salt in a 6:1 ratio only gave the 2:1 complexes apart from the case of $Co(NO_3)_2$ where a 3:1 species was precipitated after the solution had stood for some days. The complexes were washed with alcohol and ether and dried *in vacuo*. Analytical data are given in Table I.

When diethanolamine was added to solutions of metal salts in alcohol in a 2:1 ratio the complexes $[Ni(deaH)_2]Cl_2 . 2H_2O$, $[Ni(deaH)_2]Br_2 . H_2O$ and $[Cu(deaH)_2](NO_3)_2$ were precipitated in small yield. On carefully heating $[Ni(deaH)_2]Cl_2 . 2H_2O$ to 100° *in vacuo* one mole of water was lost. The filtrate from these preparations, on heating, with stirring, for 2 hours gave precipitates of the complexes $[M(dea)(H_2O)]X$ for $M = Co, Ni$, $X = Cl, Br$. If the ligand was added in a 6:1 ratio to $NiBr_2 . 3H_2O$ in ethanol or to NiI_2 in acetone (in a 2:1 ratio), no precipitation occurred, but on heating, with stirring, for 2 hours the complexes $[Ni(deaH)(dea)]X . H_2O$ ($X = I, Br$) were precipitated. Addition of the ligand in a 6:1 ratio to NiI_2 (in acetone) and $Ni(NO_3)_2$ (in ethanol), and heating for 2 hours gave a precipitate of $[Ni(deaH)_2(dea)]X . H_2O$ ($X = I, NO_3$). Addition of ligand to $CoBr_2$ in ethanol in a 6:1 ratio and standing resulted in the precipitation of $[Co(deaH)(dea]Br$. The complex $[Co(dea)H_2O](NO_3)$ was prepared by adding ligand in a 2:1 ratio to $Co(NO_3)_2 . 6H_2O$ in ethanol. All complexes were washed with alcohol and ether and dried *in vacuo*. Analytical data are contained in Table I.

Electronic spectra were measured on a Unicam SP700 instrument with a SP735 attachment for diffuse reflectance spectra. Conductivities were measured on a Doran bridge and magnetic susceptibilities on a Gouy balance. Infrared spectra were measured on Perkin Elmer 237 and Grubb Parsons DM4 spectrometers, using sodium chloride and polythene supports respectively, as nujol and HCB mulls.

Results

Complexes of N-methyldiethanolamine. These were straightforward. Table I lists the complexes with their analytical, magnetic moment and conductance data. They all are 2:1 electrolytes. Their diffuse reflectance electronic spectra and infrared spectra are

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(2) J. F. Boas, J. R. Pilbrow and T. D. Smith, *J. Chem. Soc.* (A), 723 (1969).
(3) J. L. Harvey, C. I. Tewksbury and H. M. Haendler, *J. Amer. Chem. Soc. 71*, 3641, (1949).
(4) C. W. Davies and B. N. Patel, *J. Chem. Soc.* (A) 1824 (1968).
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Table I. Analysis, Magnetic Moments and Conductivities

Complex	Colour	Λ[a]	μ[b]	Expected % C	H	N	X	M	Found % C	H	N	X	M
$[Co(medea)_2]Cl_2$	peach	220	4.68	32.6	7.10	7.60			32.6	7.09	7.63		
$[Co(medea)_2]Br_2$	peach	230	4.63	26.3	5.70	6.14			26.4	5.81	6.14		
$[Co(medea)_2]I_2$	peach	216	4.85	21.8	4.72	5.08			21.8	4.74	4.94		
$[Co(medea)_2](NO_3)_2$	peach	225	4.84	28.4	6.19	13.3			28.4	6.24	13.3		
$[Co(medea)_3](NO_3)_2$	brown	158	4.88	33.3	7.21	11.1			33.4	7.24	11.5		
$[Ni(medea)_2]Cl_2$	pale blue	222	3.28	32.6	7.12	7.63	19.1		32.5	7.13	7.63	19.2	
$[Ni(medea)_2]Br_2$	pale blue	222	3.20	26.3	5.71	6.13			26.3	6.25	6.13		
$[Ni(medea)_2]I_2$	pale blue	205	3.18	21.8	4.56	5.08			21.8	4.67	5.10		
$[Ni(medea)_2](NO_3)_2$	pale blue	216	3.28	28.3	6.18	13.3			28.4	6.20	13.5		
$[Cu(medea)_2](NO_3)_2$	green	—	2.18	28.3	6.10	13.2			28.7	5.79	10.2[c]		
$[Cu(medea)(H_2O)]Cl_2$	green	—	2.14	22.1	5.52	4.97			22.4	4.62	5.00		
$[Ni(deaH)_2]Cl_2 . 2H_2O$	blue	286		25.6	6.92	7.45			25.8	7.01	7.44		
$[Ni(deaH)_2]Br_2 . H_2O$	blue	239		21.5	5.37	6.27			21.5	5.08	6.08		
$[Ni(deaH)_2]Cl_2 . H_2O$	blue						correct weight loss						
$[Cu(deaH)_2](NO_3)_2$	pale blue	—	2.16	20.4	4.67	14.1			20.6	5.76	10.3[c]		
$[Ni(dea)(H_2O)]Cl$	apple green	104	3.29	22.3	5.55	6.49	16.4	27.2	22.9	5.17	6.57	16.6	27.1
$[Ni(dea)(H_2O)]Br$	apple green	110	3.39	18.0	4.49	5.21	30.7	22.6	19.2	4.60	5.52	30.6	22.5
$[Co(dea)(H_2O)]Cl$	purple	127	4.94	22.3	5.57	6.5	16.4		23.1	5.64	6.72	16.7	
$[Co(dea)(H_2O)]Br$	purple	116	5.00	18.0	4.98	5.21	30.7		19.1	4.60	5.34	30.5	
$[Co(dea)(H_2O)]NO_3$	blue green	—	—	19.8	4.94	11.54			20.1	4.25	10.9		
$[Ni(deaH)(dea)]Br . H_2O$	pale blue	74	3.10	26.3	6.03	7.63	21.9	16.1	26.7	5.71	7.43	21.5	15.9
$[Ni(deaH)(dea)]I . H_2O$	pale blue	102	3.16	23.3	5.57	6.79		14.2	23.4	5.64	6.77		14.5
$[Co(deaH)(dea)]Br$	dark green	71	4.31	27.6	6.02	8.06			27.7	5.53	8.10		
$[Ni(deaH)_2)(dea)]I . H_2O$	light blue	108	—	26.8	6.30	7.80			26.8	6.10	7.89		
$[Ni(deaH)_2(dea)]NO_3 . H_3O$	light blue	141	3.31	31.4	7.5	12.4			31.5	7.8	12.4		

[a] 10^{-3} *M* aqueous solutions. [b] Room temperature. [c] Nitrogen analyses for nitrates are poor.

Table II. Electronic and Infrared Spectra of N-methyldiethanolamine Complexes.

Complex	$\nu_{OH}(cm^{-1})$	$\delta_{OH}(cm^{-1})$	Electronic spectra (kK)
$[Co(medea)_2]Cl_2$	3070(s)	1005(m)	22.28(s), 20.5(s), 17.8(sh), 10.1(sh), 8.9(m)
$[Co(medea)_2]Br_2$	3070(s)	1005(m)	22.28(s), 20.5(s), 17.6(sh), 10.2(sh), 8.6(m)
$[Co(medea)_2]I_2$	3140(s)		22.3(s), 20.5(s), 17.8(m), 10.3(sh), 8.6(m)
$[Co(medea)_2](NO_3)_2$	3100(s)	1010(s)	22.5(s), 20.5(s), 17.7(sh), 10.3(sh), 8.6(m)
$[Co(medea)_3](NO_3)_2$	3400(m.br)	1075(m) 1000(w)	20.4(s), 19.4(s), 15.0(m) 8.7(m)
$[Ni(medea)_2]Cl_2$	3020(s)	1008(s)	26.07(s). 15.79(s). 10.56(s)
$[Ni(medea)_2]Br_2$	3100(m)	1005(s)	26.08(s), 15.78(s), 10.60(s)
$[Ni(medea)_2]I_2$	3160(s)	1008(m)	26.4(s), 15.73(s), 10.56(s)
$[Ni(medea)_2](NO_3)_2$	3110(s)	1015(s)	26.3(s), 15.7(s), 10.55(s)
$[Cu(medea)_2](NO_3)_2$	3170(m)	1000(m)	13.6(s), 10.5(sh)
$[Cu(medea)H_2O]Cl_2$	*	985(w)	14.26(s), 10.6(sh)

* broad band at 3300 cm^{-1} and at 1615 cm^{-1} due to water.

given in Table II. Complexes of cobalt(II) and nickel(II) ($[M(medea)_2]X_2$; M = Co, Ni, X = Cl, Br, I, NO_3, and $[Co(medea)_3](NO_3)_2$) are all of octahedral stereochemistry as indicated by their electronic spectra and magnetic moments. The independence of electronic spectra upon the nature of the anion confirms the non-coordination of the anion in the nickel(II) and the 1:2 cobalt(II) complexes. The infrared spectrum of the nitrate group is also that of ionic nitrate. In $[Co(medea)_3](NO_3)_2$ the ligand must be bidentate, with a free OH group, and in the other examples it must be terdentate.

The band positions in the electronic spectra of the nickel complexes are intermediate between those of $[Ni(en)_3]^{2+}$ and $[Ni(H_2O)_6]^{2+}$ as expected, with the $^3T_{2g} \leftarrow {}^3A_{2g}$ transition occurring at 10,500 cm^{-1}. There is no splitting of the bands and these spectra may be readily assigned in O_h symmetry. The value of B, the Racah parameter, is 749 cm^{-1}.

Two copper(II) complexes were prepared, $[Cu(medea)_2](NO_3)_2$ and $Cu(medea)(H_2O)Cl_2$, both having normal magnetic moments. The electronic spectrum of the nitrate was consistent with a distorted octahedral stereochemistry, while the infrared spectrum indicates ionic nitrate groups and the absence of $\nu_{OH(free)}$ (see below). It appears that the ligand is terdentate in this case. We were unable to ascertain if the chloride ions were coordinated in the second complex. The infrared spectrum suggested the presence of coordinated water and coordinated OH. Probably the complex is square planar.

These results are confirmed by a study of the ν_{OH} frequency. In the free ligand this occurs at 3340 cm^{-1}. In all cases where the ligand appears to be terdentate the band has shifted to the range 3170-3070 cm^{-1}, confirming coordination of the OH group. In $[Co(medea)_3](NO_3)_2$ a much broader band occurs at 3300 cm^{-1}, probably due to free and coordinated OH groups. The δ_{OH} mode in the ligand has been assigned at 1090 cm^{-1}. This is shifted in the spectra

Table III. Electronic Spectra of Complexes of Diethanolamine.

Complex	Electronic Spectra (kK)
$[Ni(deaH)_2]Cl_2 . 2H_2O$	25.3(s), 16.4(s), 10.0(s)
$[Ni(deaH)_2]Br_2 . H_2O$	25.5(s), 16.4(s). 10.1(s)
$[Ni(deaH)_2]Cl_2 . H_2O$	25.5(s), 16.4(s). 10.1(s)
$[Cu(deaH)_2](NO_3)_2$	14.1(s), 8.7(s)
$[Ni(dea)(H_2O)]Cl$	24.2(s), 19.9(w), 14.8(s), 12.45(sh), 8.6(s), 7.3(sh)
$[Ni(dea)(H_2O]Br$	24.0(s), 18.8(w), 14.8(s), 12.9(sh), 8.7(s), 7.3(sh)
$[Co(dea)(H_2O)]Cl$	20.4(sh), 19.0(s), 17.8(hs), 15.1(m), 7.85(s), 6.97(sh)
$[Co(dea)H_2O)]Br$	20.0(sh), 19.0(s), 17.8(sh), 15.2(m), 7.95(s), 6.75(sh)
$[Ni(deaH)(dea)]Br . H_2O$	24.9(s), 16.3(s), 14.8(sh), 10.5(sh), 9.0(s)
$[Ni(deaH)(dea)]I . H_2O$	25.4(s), 18.45(s), 16.4(s), 11.0(m), 8.67(m)
$[Ni(deaH)_2(dea)]I . H_2O$	24.9(s), 16.2(s), 9.0(s)
$[Ni(deaH)_2(dea)]NO_3 . H_2O$	25.7(s), 16.5(s), 10.8(sh), 8.8(s)
$[Co(deaH)(dea)]Br$	16.20(s), 8.2(s)
$[Co(dea)(H_2O)]NO_3$	22.7(sh), 16.6(s), 8.06(m)

Table IV. Infrared Spectra of Diethanolamine Complexes (cm^{-1})

Complex	$\nu_{OH(free)}$	$\nu_{OH}(H_2O)$	ν_{NH} $\nu_{OH(coord)}$	$\delta_{OH(coord)}$	$\delta_{(free)}$
$[Ni(deaH)_2]Cl_2 . H_2O$	—	3360(s)	3195(m), 3170(m)	1010(s) 990(sh)	—
$[Ni(deaH)_2]Br_2 . H_2O$	—	3400(m)	3230(m), 3180(m)	1000(m) 980(m)	—
$[Ni(deaH)_2]Br_2$	—	—	3210(m), 3160(m)	1000(m) 980(m)	—
$[Cu(deaH)_2](NO_3)$ [a]	3520(m)	—	3210(s), 3195(s)	1030(s)	1100(s)
$[Co(dea)(H_2O)]Cl$	—	3450(m,br)	3280(m), 3260(m)	995(s) 975(sh)	—
$[Co(dea)(H_2O)]Br$	—	3450(m,br)	3250(m,br)	990(s)	
$[Ni(dea)(H_2O)]Cl$	—	3450(m,br)	3260(m), 3180(m)	990(s) 970(sh)	
$[Ni(dea)(H_2O)]Br$	—	3400(m,br)	3200(m,br)	975(m)	
$[Co(dea)(H_2O)]NO_3$	—	3400(s)	3180(m,br)	1035 1000(sh)	
$[Co(deaH)(dea)]Br$ [a]	3350(m)	—	3205(m), 3105(m)	1010(s) 985(m)	1100(s)
$[Ni(deaH)(dea)]Br . H_2O$	—	3450(m,sh)	3190(s), 3170(s)	990(m) 970(m)	
$[Ni(deaH)(dea)]I . H_2O$	—	3400(m,sh)	3270(s), 3180(s)	995(s) 970(m)	
$[Ni(deaH)_2(dea)]I . H_2O$ [b]				985(s)	1090(m)
$[Ni(deaH)_2(dea)]NO_3 . H_2O$ [c]				985(s) 975(sh)	1080(m)

[a] In both complexes a weak band is observed at 1620 cm^{-1} which we assign to $\delta_{NH(coordinated)}$. [b] 3400(m,sh), 3320(m,sh), 3260(m), 3190(m). [c] 3400(m,br,sh), 3300(sh), 3270(m), 3240(m)

of the complexes down to 1010 cm^{-1}, but in the spectrum of $[Co(medea)_3](NO_3)_2$ there are bands at 1075 and 1000 cm^{-1}, again confirming the presence of free and coordinated OH grups. The absence of bands due to free OH confirms $[Cu(medea)_2](NO_3)_2$ to be 6-coordinate.

The far infrared spectra of these complexes were of poor quality. It was possible, however, to note that there were no halogen dependent bands in the spectra of corresponding complex chlorides, bromides and iodides.

Complexes of Diethanolamine. The preparation of the complexes $[Ni(deaH)_2]Cl_2.H_2O$, $[Ni(deaH_2]Br_2 . H_2O$ and $Ni(deaH)Cl_2 . 2H_2O$ has been reported[1], as also have dimeric species in solution work with copper (II). We have obtained complexes in which the ligand is deprotonated (dea).

Complexes with non-deprotonated ligand. We have prepared $[Ni(deaH_2]X_2H_2O$ (X = Cl, Br), $[Ni(deaH)_2]Cl_2 . 2H_2O$, $[Ni(deaH)_2]Br_2$ and $[Cu(deaH)_2](NO_3)_2$. The nickel(II) complexes are all of O_h symmetry, there being no splitting of the bands in their spectra (Table III). Values of $10D_q$ and B are 10.0 kK and 770 cm^{-1} respectively. The higher value of $10D_q$ for N-methyldiethanolamine may be attributed to the base strengthening effect of the methyl group. The complexes are all 2: 1 electrolytes and the bands in their electronic spectra are halide independent. The infrared spectrum of $[Cu(deaH)_2](NO_3)_2$ shows the presence of ionic nitrate groups.

The ligand is terdentate in the nickel(II) complexes and probably bidentate in the copper complex, as indicated in the latter case by the presence of bands in the infrared spectrum which we have assigned to ν_{OH} and δ_{OH} of the free group. The complex $[Ni(deaH)_2]Br_2$ was prepared by the careful heating of the hydrate in vacuum. Its infrared spectrum was of value for comparison purposes.

Complexes $[M(dea)(H_2O)]X$; $M = Ni$, $X = Cl$, *Br; M = Co, X = Cl, Br, NO_3.* Conductance values for these complexes (104-127 ohm^{-1} cm^{-2}) are in the range observed for 1:1 electrolytes in aqueous solution, while their electronic spectra are halide independent. The presence of water is shown in their infrared spectra (Table IV), although it is difficult to unambigously identify it as coordinated water by a consideration of the ν(O–H) region in view of the complexity of the spectra. However, all these complexes showed a number of additional bands compared to $[M(deaH)_2]X_2$, $[M(deaH)_2]X_2 . H_2O$ and other complexes in the region 1080 to 780 cm^{-1}. We assign these to coordinated water.[6] The spectra of the complex chlorides show splitting of certain bands compared with the spectra of bromides. We assume this is a solid state effect. The complexes are of octahedral stereochemistry as indicated by their magnetic moments and electronic spectra. However the spectra of the nickel complexes show strong splitting of the two lower energy bands and may be assigned in D_{4h} symmetry.[7] We have calculated values of the in-plane and axial ligand field strengths, $10Dq_{xy}$ and $10Dq_z$ to be 8.66 and 5.98 kK respectively, with $Ds =$ 423 and $Dt = 150$. The electronic spectra of the cobalt(II) complexes are similar to those of some phosphine oxide complexes of cobalt(II) nitrate known[8] to have an irregular 6-coordinate stereochemistry. Careful heating of the cobalt compexes resulted in the formation of anhydrous, dark green tetrahedral species.

We have also prepared a blue-green complex $[Co(dea)H_2O](NO_3)$, of tetrahedral stereochemistry, with an ionic nitrate group. There is no evidence for a free OH group in the infrared spectrum. The ligand appears to be terdentate.

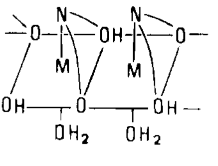
The formulation of these complexes as hydroxo complexes rather than complexes with deprotonated diethanolamine is clearly excluded by their infrared spectra.

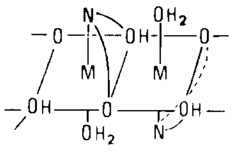
Complexes $[M(deaH)(dea)]X . nH_2O$.. These were obtained for nickel (X=Br, I, n=1) and cobalt (X=Br, n=0). All are 1: 1 electrolytes. The nickel complexes are of D_{4h} symmetry, but there are differences between bromide and iodide. The electronic spectra data allows the calculation of, for the bromide, $10Dq_{xy} = 10.5$kK, $10Dq_z = 7.51$kK, $Ds = 282$, $Dt = 171$, and for the iodide, $10Dq_{xy} = 11.0$kK, $10Dq_z = 6.34$kK, $Ds = 397$ and $Dt = 266$. Clearly there are significant differences for bromide an iodide, probably reflecting different packing in the crystal. For nickel(II) the ligand is terdentate. The cobalt(II) complex is tetrahedral with no indication of a lowering of its symmetry beyond T_d. The bidentate nature of the ligand is confirmed by the presence of a band at 3350 cm^{-1} in the infrared spectrum of the complex which we have assigned to ν_{OH} of the free OH group.

Complexes $[Ni(deaH)_2(dea)]X . H_2O(X=NO_3,I)$. These complexes are 1:1 electrolytes. Their electronic spectra may be assigned in O_h symmetry, with $10Dq = 9.0$kK, although there is some slight splitting in the lowest energy band in the spectrum of the nitrate. Here the ligand is clearly bidentate, although the presence of the water molecule prevents a firm assignment of ν_{OH}(free) in the infrared spectrum. In both cases there is a broad band at 3400 cm^{-1}. The value of $10Dq$ is lower than expected for an N,O chelating ligand and is probably due to a steric effect of the non coordinated $-CH_2CH_2OH$ group.

Conclusions. While the general behaviour of these two ligands appears to be established, we have not yet considered the site from which the proton is lost. It seems reasonable that the formation of complexes with deprotonated ligand would involve the loss of an OH proton, the prior coordination of this group facilitating this reaction. However complexes with deprotonated ligand were not formed with N-methyldiethanolamine, possibly suggesting the loss of the secondary amine proton in the case of diethanolamine. The weakness of the δ_{N-H} band in the infrared spectrum of the ligand has prevented the solution of this problem by this means. It is present in the ligand at 1650 cm^{-1} but on coordination would be lowered in frequency and masked by OH absorptions. We have observed this mode in some anhydrous complexes, but these involved deaH as a ligand. A comparison of the 3400 - 3000 cm^{-1} region for complexes of diethanolamine and N-methyldiethanolamine has allowed the observation of additional bands in the spectra of complexes of the former ligand which we tentatively assign to ν_{N-H}. However it may well be that the deprotonated complexes are not formed with N-methyldiethanolamine because of the rapid precipitation of the complexes with this ligand. In the case of diethanolamine, the complexes $[Ni(deaH_2]X_2$ were formed first in solution and only on long standing were they converted to complexes of the deprotonated ligand.

The structure of the complexes $[M(dea)(H_2O)]X$ is difficult to formulate. Both –OH and O⁻ groups must bridge metal ions. Possible structures are given below. Others may be written in which the OH groups take up a *cis*-configuration.





For the 1:2 complexes with diethanolamine and N-methyldiethanolamine it is possible to write alternative structures, depending upon whether vicinal or equatorial coordination of the ligand has taken place.

The absence of halide coordination for both ligands is of interest. It does not appear to be a steric effect as water is coordinated. In the absence of any π-acceptor donor groups, halide may be excluded from the coordination shell in order to prevent the build up of exececssive charge.

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