

Pentacoordinated Ni(Bidentate)(Tridentate) Chelates and their Hydrates

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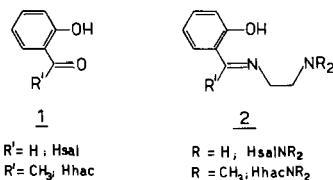
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Reaction of bis(acetylacetonato)nickel(II), $Ni(acac)_2$ (dihydrate or anhydrous), with tridentate Schiff bases (HB) in boiling toluene followed by exposure of the reaction mixture to moist air leads to the ready isolation of crystalline complexes of composition $Ni(acac)(B)(OH_2)$. Their spectral and magnetic properties are in accord with pseudooctahedral geometry. On heating, these complexes readily dehydrate giving rise to $Ni(acac)(B)$. These have infrared spectra characteristic of the mixed ligand formulation. Their electronic spectra can be readily fitted with high-spin square pyramidal geometry. In moist solvents the equilibrium between $Ni(acac)(B)$ and $Ni(acac)(B)(OH_2)$ can be identified from spectral data. The thermodynamics for this equilibrium has been studied in one case using variable temperature spectral results.

Introduction

A monomeric complex of the formula MLL' (L = bidentate, L' = tridentate) in which all the potentially coordinating atoms are bonded to the metal will be pentacoordinated. This simple strategy for the design of pentacoordination has been rarely used in practice.^{1,2} Some years ago we initiated a project based on the MLL' theme. Thus complexes of the type $Cu(sal)$ ($salNR_2$) or $Cu(hac)(hacNR_2)$ are indeed pentacoordinated with a slightly distorted



square pyramidal geometry.³ On the other hand the corresponding nickel(II) complexes are dimers and show more complicated stereochemical pattern involving both pentacoordinated and octahedral geometries.⁴ In this paper are described the results of our investigations on nickel(II) complexes of the type $Ni(acac)(salNR_2)$ where acac stands for acetylacetonate anion.

Results and Discussion

Syntheses and Characterization

When Schiff bases of the type $HsalNR_2$ (1 mole) are reacted with bis(acetylacetonato)nickel(II) (dihydrate or anhydrous) (1 mole) in boiling toluene and the resulting brown solution is left to crystallise in open air (which supplies moisture) shining green crystals of composition (Table I) $Ni(acac)(salNR_2)(OH_2)$ deposit. Alternatively $Ni(acac)(salNR_2)(OH_2)$ can be obtained by reacting $Ni(acac)_2 \cdot 2H_2O$ with $Ni(salNR_2)_2$ or $Ni(salNR_2)_2$ with Hhacac in equimolecular amounts in boiling toluene followed by open air crystallization. When heated in the range 80–100° at 5 mm the green crystals slowly disintegrate to a brown mass which when cooled becomes a glassy solid. During this process water is lost, the maximum loss corresponding to one mole of water per mole of the complex. The composition of glassy mass is found to be $Ni(acac)(salNR_2)$. When this is recrystallized from moist solvents the crystals of $Ni(acac)(salNR_2)(OH_2)$ are regenerated. From solvents containing pyridine (py) crystals of $Ni(acac)(salNR_2)(py)$ can be readily obtained. When $HsalNR_2$ is replaced by $HhacNR_2$ similar results are obtained. The complexes have compositions $Ni(acac)(hacNR_2)(OH_2)$ and $Ni(acac)(hacNR_2)$.

The molecular weights of one complex, viz., $Ni(acac)(salNEt_2)(OH_2)$ and its anhydrous form were determined cryoscopically in pure benzene in presence of partially hydrated sodium sulphate which keeps the concentration of water in benzene invariant.⁵ The observed molecular weight 375 ± 20 lies very close to that calculated for $Ni(acac)(salNEt_2)$ (377).

The complexes give rise to characteristic infrared spectra. The hydrates show the expected ν_{O-H} frequency at $\sim 3430\text{ cm}^{-1}$ (Table II). This band is absent in the anhydrous compounds and in the pyridine adducts. All the complexes show a strong band in the region 1600–1630 cm^{-1} assigned to $\nu_{C=N}$ of the Schiff base moiety. There are two strong bands in the range 1590–1600 cm^{-1} and 1505–1515 cm^{-1} which are probably due to the combination of $\nu_{C=C}$ and $\nu_{C=O}$ stretches of the acac moiety⁶ with additional contributions from aromatic vibrations of Schiff base.

TABLE I. Characterization data^a

Compound	Mp, °C ^b	% C		% H		% N		% Ni		% H ₂ O	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Ni(acac)(salNMe ₂)(OH ₂)	180–182	52.34	52.53	6.59	6.36	7.63	7.44	16.00	15.90	4.90	4.50
Ni(acac)(salNEt ₂)(OH ₂)	104–105	54.71	54.44	7.14	7.14	7.09	7.20	14.86	14.95	4.55	4.59
Ni(acac)(5-Cl-salNEt ₂)(OH ₂)	143–145	50.20	50.29	6.55	6.59	6.50	6.60	13.63	13.50	4.18	4.08
Ni(acac)(salN- <i>n</i> -Bu ₂)(OH ₂)	96–97	58.57	58.88	8.04	7.80	6.21	6.36	13.01	12.91	3.99	4.10
Ni(acac)(hacNMe ₂)(OH ₂)	216–217	53.59	53.83	6.87	6.61	7.34	7.53	15.41	15.40	4.72	4.59
Ni(acac)(hacN- <i>n</i> -Bu ₂)(OH ₂)	99–100	59.38	59.30	8.23	8.20	6.02	6.11	12.62	12.74	3.87	c

^a Nickel analysis for other compounds: Ni(acac)(salNMe₂)py: calcd, 13.71; found, 13.77. Ni(acac)(salNMe₂): calcd, 16.82; found, 16.82. Ni(acac)(salNEt₂): calcd, 15.56; found, 15.53. Ni(acac)(5-Cl-salNEt₂): calcd, 14.23; found, 14.05.
^b All melting points are uncorrected. ^c Not determined.

TABLE II. Solid state data of monohydrated complexes.^a

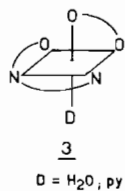
Compound	Infrared frequencies (cm ⁻¹) ^b ν _{C=N} ν _{C=O} + ν _{C=C} + ν _{aromatic}	Magnetic moment (BM) μ _{eff}	Electronic spectra: band positions (cm ⁻¹)	
			³ A _{2g} (F) → ³ T _{2g} (F)	→ ³ T _{1g} (F)
Ni(acac)(salNMe ₂)(OH ₂)	1630	3.26	11,100	16,950
Ni(acac)(salNEt ₂)(OH ₂)	1625	3.15	10,530	16,670
Ni(acac)(5-Cl-salNEt ₂)(OH ₂)	1625	3.19	10,500	16,800
Ni(acac)(salN- <i>n</i> -Bu ₂)(OH ₂)	1624	3.16	10,300	16,980
Ni(acac)(hacNMe ₂)(OH ₂)	1600	3.29	11,100	16,550
Ni(acac)(hacN- <i>n</i> -Bu ₂)(OH ₂)	1600	3.17	11,100	16,950
Ni(acac)(salNEt ₂)(py)	1610	c	13,000	17,950

^a The data given in this table is recorded at room temperature. ^b All the compounds have a broad band at 3425 cm⁻¹ due to ν_{H₂O} except the anhydrous compounds and their pyridine adducts. ^c Measurement not made.

Structure in the Solid State

Hydrates

The monohydrates are fully paramagnetic in the solid state (Table II) and obey Curie-Weiss law over the range -170 to $+30^\circ$. Their electronic spectra are clearly in accord with pseudooctahedral geometry (Table II). The ligand field spectrum of the pyridine adduct $\text{Ni}(\text{acac})(\text{salNEt}_2)(\text{py})$ also follows the same pattern. Most probably the hydrates and pyridine adducts belong to the type 3.



Anhydrous compounds

The electronic spectra (Figure 1, Table III) of anhydrous compounds taken as films are quite different from the spectra of the hydrates. The distinguishing feature is at $\sim 7300 \text{ cm}^{-1}$. The observed spectra reveal the occurrence of pentacoordinated geometry in most certain terms. On the basis of our earlier investigations on $\text{Cu}(\text{sal})(\text{salNR}_2)^{3,7}$ and the corresponding dimeric nickel(II) species⁴ we strongly believe that the anhydrous compounds have the high-spin pentacoordinated square pyramidal structure 4. There is

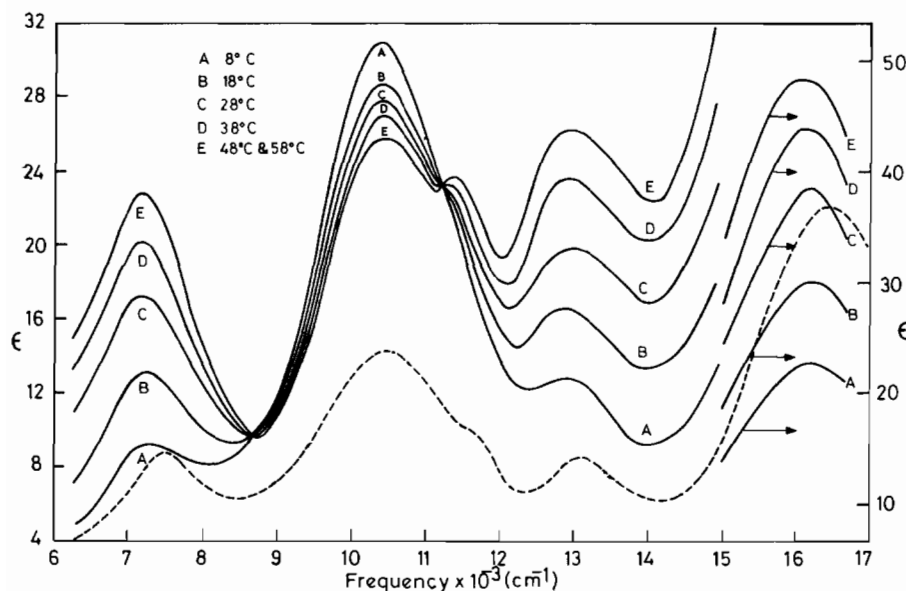
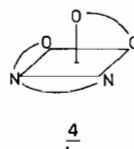


Figure 1. Variable temperature electronic spectra of $\text{Ni}(\text{acac})(\text{salNEt}_2)(\text{OH}_2)$ in benzene solute concentration $\sim 1.8 \times 10^{-2} \text{ mole l}^{-1}$, (----), thin film spectrum of $\text{Ni}(\text{acac})(\text{salNEt}_2)$, the ordinate is absorbance in arbitrary units.

TABLE III. Electronic spectra of anhydrous compounds in thin films.

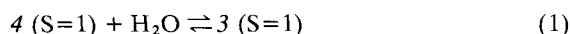
Compound	Assignments ^a of band positions (cm^{-1})				
	${}^3\text{B}_1(\text{F}) \rightarrow {}^3\text{E}(\text{F})$	$\rightarrow {}^3\text{A}_2(\text{F})$	sft ^b	$\rightarrow {}^3\text{B}_2(\text{F})$	$\rightarrow {}^3\text{E}(\text{F})$
Idealised square pyramid ^c ; $\beta^d = 100^\circ, \mu = 4.89 \text{ Debye}$	7150	10,900	—	12,550	17,700
$\text{Ni}(\text{acac})(\text{salNMe}_2)$	7350	10,600	11,500 ^e	13,000	16,300
$\text{Ni}(\text{acac})(\text{salNEt}_2)$	7450	10,500	11,600 ^e	13,100	16,500
$\text{Ni}(\text{acac})(5\text{-Cl-salNEt}_2)$	7300	10,500	11,600 ^e	13,000	16,800
$\text{Ni}(\text{acac})(\text{hacNMe}_2)$	7100	10,600 ^e	11,600	13,000	16,700
$\text{Ni}(\text{acac})(\text{hacN-}n\text{-Bu}_2)$	7150	10,500	11,550	13,000	16,600

^a The assignments printed in ref. 9 have typographical errors. ^b Spin forbidden transition. ^c Calculated on the basis of Ciampolini diagram⁸ for idealized C_{4v} geometry. ^d The angle between axial and one of the basal bonds. ^e Shoulder.

good accord between observed crystal field frequencies and those calculated using Ciampolini model for pyramidal geometry⁸ (Table III).

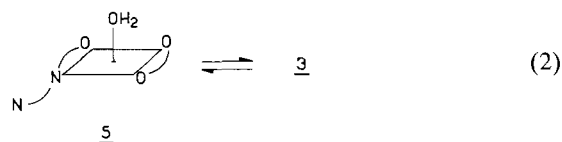
Equilibria in Solution

The qualitative nature of solution spectra of these complexes in benzene is similar to that of the anhydrous complexes in the solid state. The case of Ni(acac)(salNET₂) is illustrated in Figure 1. Structure 4 thus makes a major contribution to solution composition. However, the solution spectra are dependent on concentration of water present and on the temperature. The intensities of ~7000, ~13,000 and ~16,500 cm⁻¹ bands decrease with (i) increasing concentration of water,⁹ and (ii) decreasing temperature (Figure 1). On the other hand the band at ~10,500 cm⁻¹ behaves in the opposite fashion (Figure 1). Variable temperature spectra (Figure 1) are strictly reversible and are characterized by good isosbestic points. The observed results can be readily interpreted in terms of eqn. (1) which shifts



to the right with increasing concentration of water and/or decreasing temperature. The ³A_{2g} → ³T_{2g} transition of 3 and ³B₁ → ³A₂ transition of 4 are superposed at ~10,500 cm⁻¹. With a shift of the above equilibrium to the right intensity of the observed band increases because ε(³A_{2g} → ³T_{2g}) > ε(³B₁ → ³A₂). Similarly, the band at ~16,500 cm⁻¹ contains both octahedral ³A_{2g} → ³T_{1g} and square pyramidal ³B₁ → ³E transitions. The observed changes in intensity can be rationalised if ε(³A_{2g} → ³T_{1g}) < ε(³B₁ → ³E). The most convincing evidence for the occurrence of the equilibrium lies with the band at ~7000 cm⁻¹ which is due to the pentacoordinated species alone.

The observed dependence of the spectra⁹ on the concentration of water excludes the occurrence of an alternative square pyramidal (5) – octahedral (3) equilibrium in which bonding to water remains intact



(equation (2)). The solution magnetic moments of Ni(acac)(salNET₂)(OH₂) and other hydrates are given in Table IV. The most significant point to note is that between 25 and 70° the observed magnetic moments consistently show the occurrence of high-spin nickel(II) species only. This is understandable providing the equilibrium (1) alone describes the solution composition. In order to determine the thermodynamics of the equilibrium (1) the variable temperature spectra of Ni(acac)(salNET₂)(OH₂) were studied in anhydrous benzene (Figure 1) and benzene containing a known concentration of water. The intensity of the ~7000 cm⁻¹ band was taken as an index of the population of the pentacoordinated species. The values of ΔH° and ΔS° are found to be (see Experimental Section)

$$\Delta H^\circ = -13 \pm 1 \text{ kcal mole}^{-1}$$

$$\Delta S^\circ = -36 \pm 5 \text{ eu}$$

In literature we did not find other examples of stereochemical equilibria between octahedral and pentacoordinated complexes brought about by reversible dissociation of a water molecule. There are some examples where such equilibria are observed as a result of reversible adduct formation with pyridine.^{10,11}

The behaviour of other complexes in solution is similar to that of Ni(acac)(salNET₂)(OH₂). In a given solvent at a given temperature the population of the pentacoordinated species as measured by the intensity of the ~7000 cm⁻¹ band follows the order Ni(acac)(salNET₂)(OH₂) ~ Ni(acac)(hacN-*n*-Bu₂)(OH₂) > Ni(acac)(salN-*n*-Bu₂)(OH₂) > Ni(acac)(5-Cl-salNET₂)(OH₂) > Ni(acac)(hacNMe₂)(OH₂) > Ni(acac)(salNMe₂)(OH₂) (Table V). For a given compound the population of pentacoordinated species in different

TABLE IV. Solution magnetic moments (μ_{eff} , BM) of monohydrated complexes.^a

Compound	Benzene			Chloroform		
	Temperature °C	Concentration mole l ⁻¹ x 10 ²	μ_{eff}	Temperature °C	Concentration mole l ⁻¹ x 10 ²	μ_{eff}
Ni(acac)(salNET ₂)(OH ₂)	25		3.27	25		3.24
	40	5.84	3.26	40	6.78	3.24
	55		3.26	56		3.24
	70		3.30			
Ni(acac)(5-Cl-salNET ₂)(OH ₂)		b		29	5.49	3.30
Ni(acac)(salN- <i>n</i> -Bu ₂)(OH ₂)	27	5.51	3.18	26	5.48	3.24
Ni(acac)(hacN- <i>n</i> -Bu ₂)(OH ₂)	26	4.74	3.26	25	5.46	3.26

^a Measurements were made where solubility permitted. ^b Insufficiently soluble in benzene.

TABLE V. Frequencies (ν , cm^{-1}) and extinction coefficients (ϵ , $1 \text{ mole}^{-1} \text{ cm}^{-1}$)^a of the 7000 cm^{-1} band at room temperature.

Compound	Solvent	ν	ϵ
Ni(acac)(salNMe ₂)(OH ₂)	Chloroform	7000	14.7
Ni(acac)(salNEt ₂)(OH ₂)	Benzene	7200	17.2
	Chloroform	7150	22.5
	Nitrobenzene	7200	22.0
Ni(acac)(5-Cl-salNEt ₂)(OH ₂)	Benzene	7200	14.0
	Chloroform	7200	17.5
Ni(acac)(salN- <i>n</i> -Bu ₂)(OH ₂)	Benzene	7200	15.0
	Chloroform	7200	22.0
	Nitrobenzene	7200	21.5
Ni(acac)(hacNMe ₂)(OH ₂)	Chloroform	7000	17.0
Ni(acac)(hacN- <i>n</i> -Bu ₂)(OH ₂)	Benzene	7200	17.0
	Chloroform	7200	17.7
	Nitrobenzene	7100	19.0

^a Solute concentrations are $\sim 1.5 \times 10^{-2} \text{ mole l}^{-1}$.

solvents has the order benzene < chloroform \sim nitrobenzene (Table V).

Concluding Remarks

The MLL' strategy for obtaining pentacoordinated complexes has worked well with the complexes described in this paper. The hindering effect comes from the adduct formation. The behaviour of the present complexes is to be contrasted with that of the dimeric Ni₂(sal)₂(salNR₂)₂ species. The observed pattern can now be rationalised if the phenolic oxygen of the sal unit is considered to be a better bridging atom than the β -diketonate oxygen of the acac unit.

Experimental Section

Preparation of Compounds

Bis(acetylacetonato)nickel(II) dihydrate and its anhydrous analogue were prepared by published procedures.^{12, 13}

Synthesis of Ni(acac)(salNR₂)(OH₂)

These complexes were prepared by the following three general procedures.

(a) Reaction of Ni(acac)₂ with Schiff bases

2.6 g of Ni(acac)₂ (0.01 mole) and the Schiff base (0.01 mole) were taken in 50 ml of toluene. The mixture was heated to reflux for 2 hr. During this period the solution, initially green, turned brown. In the case of Ni(acac)(salNMe₂)(OH₂) the solution was filtered and concentrated (20 ml) and left to cool in air. Green crystals deposited in 60% yield. The other complexes did not separate from toluene. Two alternative procedures were used to isolate solid crystals. (i) Toluene was

completely removed at a reduced pressure and the residue was dissolved in ethanol; on adding water, the green crystals were obtained. (ii) The volume of toluene was reduced to 10 ml and hexane (30 ml) was added; on keeping in air, the green crystals were obtained in 50% yield. These compounds were recrystallized either from ethanol-water or from toluene-hexane mixtures. Similar results were obtained when Ni(acac)₂ · 2H₂O in place of Ni(acac)₂ was used. The complexes Ni(acac)(hacNR₂)(OH₂) were prepared by a similar procedure.

(b) Reaction of Ni(acac)₂ with Ni(salNR₂)₂

2.6 g of Ni(acac)₂ (0.01 mole) and Ni(salNR₂)₂ (0.01 mole) were taken in 50 ml of toluene. The mixture was heated to reflux for 2 hr. The solution was treated further as described in (a) to obtain the crystalline complexes.

(c) Reaction of Ni(salNR₂)₂ with acetylacetonate

To a solution of Ni(salNR₂)₂ (0.01 mole) in 50 ml toluene was added 1 g (0.01 mole) of acetylacetonate. The mixture was heated to reflux for 2 hr. The solution was treated further in a similar way as described in (a) to obtain the crystalline complexes.

Ni(acac)(salNR₂)

The Ni(acac)(salNR₂)(OH₂) were heated at 80° (5 mm) for 4–6 hr. The crystals scrambled to a brown glassy mass losing water of crystallization. These glassy masses when recrystallized as described in (a) gave back Ni(acac)(salNR₂)(OH₂).

Physical Measurements

Magnetic moments were studied using a sensitive Gouy balance described elsewhere.¹⁴ Infrared spectra were recorded on a Perkin-Elmer 521 recording spectrophotometer. Molecular weight was determined cryoscopically in purified dry benzene.⁵ Electronic spectra were studied on a Cary Model 14 recording spectrophotometer. The solid monohydrated compounds were examined in nujol mulls. The films of anhydrous compounds were prepared as follows. Approximately 0.1 g of monohydrated complex was placed on the quartz plate which was gently heated on a hot plate until the compound started to melt. It was removed quickly and another identical quartz plate made a little hot was placed over the sample giving a transparent brown film. Such films were used to record the spectra. Variable temperature solution measurements were made by circulating thermostated ($\pm 0.1^\circ$) water or 95% ethanol through an appropriate cell holder.

Calculation of Thermodynamic Parameters

Let x , $(w+x)$ and $(a-x)$ be the equilibrium concentrations of pentacoordinate species, water and octahedral species. Here w is the concentration of water

TABLE VI. Thermodynamic data on the equilibrium from ligand field spectrum in benzene for Ni(acac)(salNEt₂)(OH₂).

Temperature °C	a × 10 ^{2a} mole l ⁻¹	w × 10 ^{2 a, b} mole l ⁻¹	ε ^a l mole ⁻¹ cm ⁻¹	K ^a	log K
8	1.846	—	9.2	198.5	2.30
18	1.825	—	13.2	68.8	1.84
28	1.796	—	17.2	24.0	1.38
30	2.714	3.642	10.5	24.0	1.38
40	2.680	3.596	12.7	21.0	1.32
50	2.648	3.553	16.6	6.8	0.83
70	2.581	3.463	19.7	2.8	0.44

^aThe symbols in this table have the same meaning as in equation (1) and (4). ^bw stands for the concentration of water added externally at 30°, the remaining concentrations were calculated by applying the volume corrections.

added externally. It follows from equation (1) that equilibrium constant (K)

$$K = \frac{a-x}{x(w+x)} \quad (3)$$

Let the intensity of the ~7000 cm⁻¹ band be ε₀ when the whole of the complex is in the form of 5. The observed intensity ε is then related to x as

$$x = a\epsilon/\epsilon_0 \quad (4)$$

Combining (3) and (4) one obtains

$$K = \frac{1-\epsilon/\epsilon_0}{(a\epsilon/\epsilon_0)(a\epsilon/\epsilon_0 + w/a)} \quad (5)$$

The limiting value ε₀ is taken as 22.81 l mole⁻¹ cm⁻¹ since the intensity did not increase beyond this value in anhydrous benzene (Figure 1). The data are collected in Table VI. The enthalpy and entropy changes ΔH° and ΔS° are related to K by the well-known equation,

$$\Delta H^\circ/T - \Delta S^\circ = -R \ln K \quad (6)$$

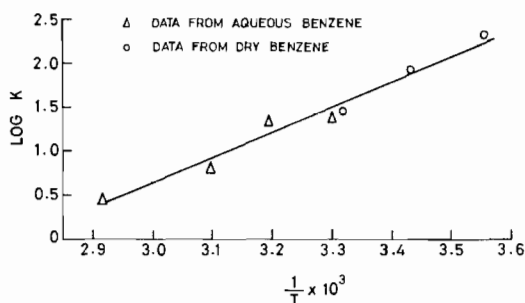


Figure 2. Log K versus T^{-1} plot for Ni(acac)(salNEt₂)(OH₂) using spectral data in benzene (Table VI).

From the least square plot of equilibrium constant versus temperature (Figure 2) the values of ΔH° and ΔS° were calculated by using the relation (6).

Acknowledgement

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