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Complexes of Nickel(II) with Acetonitrile. Coordination of Perchlorate

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Three coordination compounds of acetonitrile with nickel(II) perchlorate have been prepared and characterized as $[Ni(CH_3CN)_6](ClO_4)_2$, $[Ni(CH_3CN)_4(ClO_4)_2]$, and $[Ni(CH_3CN)_2(ClO_4)_2]$. The infrared spectra between 1000 and 1200 cm.$^{-1}$ clearly indicate the presence of monodentate perchlorato groups in $[Ni(CH_3CN)_4(ClO_4)_2]$ and of bidentate perchlorato groups in $[Ni(CH_3CN)_2(ClO_4)_2]$. Dq, χ, B', and λ have been evaluated for each of the compounds.

Introduction

To date, no detailed study has been made of the coordination compounds of acetonitrile with nickel(II). One complex, $Ni(CH_3CN)_{3.5}Cl_2$,[2] has been isolated, but has not been completely characterized.

During the course of this investigation of acetonitrile complexes of nickel(II) perchlorate, perchlorate was observed to enter the coordination sphere. Relatively few such examples have been recorded. Moore, Gayhart, and Bull[3] have observed perchlorate coordination in nickel(II) complexes with substituted pyridines. Hathaway, Holah, and Hudson[4] have observed coordination of perchlorate in the dihydrate of nickel(II) perchlorate, while Harris and McKenzie[5] suggest the weak coordination of perchlorate in $Ni(o\text{-phen})_2(ClO_4)_2$.

This paper reports complexes of nickel(II) perchlorate with acetonitrile and the coordination of perchlorate ion in these compounds.

Experimental

Hexaaquonickel(II) Perchlorate.—$HClO_4$ (130 ml. of 70% acid) was added dropwise with stirring to a slurry of 85 g. (0.75 g.-ion of Ni^{+2}) of $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ in 200 ml. of water. After filtration, the product was isolated by evaporating the solution on a steam bath until crystallization started, cooling in ice, and filtering. Four crops of crystals were obtained, washed with a small portion of ice–water, and dried *in vacuo* over P_2O_5; yield 340 g. (90%).

Acetonitrile.—Eastman anhydrous grade acetonitrile was dried by distillation from P_2O_5.

Nitromethane.—Nitromethane was shaken twice with Drierite and distilled. The fraction boiling between 99.2 and 102° was retained.

Diethyl Ether.—Mallinckrodt anhydrous ether was further dried by shaking with anhydrous $MgSO_4$.[6] It was stored over $MgSO_4$ and filtered immediately before use.

Magnesium Sulfate.—$MgSO_4 \cdot 7H_2O$ was dried at 250° for 48 hr.; the crust was broken up several times during the drying.

Hexakis(acetonitrile)nickel(II) Perchlorate.—$[Ni(H_2O)_6](ClO_4)_2$ (15 g.) was dissolved in 200 ml. of acetonitrile and stirred with two 10-g. portions of P_2O_5. After decanting, the solution was stirred with three more 10-g. portions of P_2O_5. The dark blue solution was refluxed 1.5 hr. with an additional 15 g. of P_2O_5. The mixture, now dark green, was rapidly filtered into 100 ml. of anhydrous ethyl ether, causing precipitation of a light purple powder from a dark yellow solution. The flask was immediately closed to the atmosphere and transferred to a glove bag containing a dry nitrogen atmosphere. There the product was recrystallized twice by dissolving in 50 ml. of dried acetonitrile and precipitating with 100 ml. of anhydrous ether. After washing with ether, the product, protected by a P_2O_5 drying tube, was dried *in vacuo* at 30° for 15 hr.; yield 10.37 g. (54.4%).

Anal. Calcd. for $[Ni(CH_3CN)_6](ClO_4)_2$: C, 28.59; H, 3.58; N, 16.69; Cl, 14.10. Found: C, 28.56; H, 3.81; N, 16.39; Cl, 14.15.

Attempts to Prepare Anhydrous $[Ni(CH_3CN)_6](ClO_4)_2$.—Evaporation of an acetonitrile solution of $[Ni(H_2O)_6](ClO_4)_2$ gave a blue solid which contained 2–3 moles of water. A number of drying agents were used in attempting to remove this water.

2,2-Dimethoxypropane.—Dimethoxypropane has been used successfully to prepare a number of anhydrous complexes from hydrated salts.[7] $[Ni(H_2O)_6](ClO_4)_2$ and $[Ni(CH_3CN)_x(H_2O)_y](ClO_4)_2$ were stirred with an excess of dimethoxypropane at room temperature. In both cases, on addition of CH_3CN and ether, blue oils were formed. Repeated extraction with ether sometimes caused a solid to form which showed O–H on infrared examination.

Refluxing the starting materials with dimethoxypropane and distilling off the acetone and methanol produced did not yield the anhydrous complex.

Bis(perchlorato)tetrakis(acetonitrile)nickel(II).—In the glove bag, 1.4902 g. of $[Ni(CH_3CN)_6](ClO_4)_2$ was placed in a tared tube connected by a ground-glass joint to a stopcock. The sample was heated *in vacuo* at 65° until it was entirely blue (20 hr. for this sample, less for smaller quantities). Weight loss was monitored during the reaction, and heating was stopped when the loss corresponded to the removal of 2 moles of acetonitrile.

Anal. Calcd. for $[Ni(CH_3CN)_4(ClO_4)_2]$: C, 22.72; H, 2.84; N, 13.24; Cl, 16.81. Found: C, 22.61; H, 3.01; N, 13.59; Cl, 16.76.

Bis(perchlorato)bis(acetonitrile)nickel(II).—Using the same apparatus as above, 1.3245 g. of $[Ni(CH_3CN)_6](ClO_4)_2$ was heated *in vacuo* at 75° for 28 hr.; green $[Ni(CH_3CN)_2(ClO_4)_2]$ was obtained.

Anal. Calcd. for $[Ni(CH_3CN)_2(ClO_4)_2]$: C, 14.11; H, 1.76; N, 8.25; Cl, 20.87. Found: C, 14.22; H, 1.91; N, 7.98; Cl, 21.01.

Analysis.—Microanalyses for carbon, hydrogen, nitrogen, and chlorine were performed by Galbraith Laboratories, Inc. Special handling of the samples in a drybox was requested, as the compounds are hydrolyzed by atmospheric moisture.

Physical Measurements. Infrared Spectra.—Spectra between 2 and 15 μ were recorded on a Perkin-Elmer Model 21 spectrophotometer. Samples were mulled with Nujol and halocarbon oil in a dry nitrogen atmosphere and placed between sodium chloride plates.

Magnetic Measurements.—Magnetic susceptibilities were run on solid samples on a Gouy balance at room temperature. The

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(1) Submitted to the Graduate School of The University of Connecticut by A. E. W. in partial fulfillment of the requirements for the degree Master of Science.

(2) R. J. Kern, *J. Inorg. Nucl. Chem.*, **25**, 5 (1963).

(3) L. E. Moore, R. B. Gayhart, and W. E. Bull, *ibid.*, **26**, 896 (1964).

(4) B. J. Hathaway, D. G. Holah, and M. Hudson, *J. Chem. Soc.*, 4586 (1963).

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field was standardized at two strengths with ferrous ammonium sulfate. Samples were loaded in the Gouy tube inside a glove bag. The diamagnetic correction for acetonitrile was -21×10^{-6} c.g.s. unit per mole, using water as a standard. Diamagnetic corrections were made for Ni^{+2} and ClO_4^-.

Electronic Spectra.—A solution spectrum in acetonitrile was run on $[Ni(CH_3CN)_6](ClO_4)_2$ from 300 to 1500 mμ on a Cary Model 14 recording spectrophotometer. A solid spectrum of $[Ni(CH_3CN)_6](ClO_4)_2$ was obtained on the Cary using a Nujol mull protected by sodium chloride plates. Mineral oil saturated Kleenex were placed in the reference beam. Reflectance spectra of $[Ni(CH_3CN)_4(ClO_4)_2]$ and $[Ni(CH_3CN)_2(ClO_4)_2]$ were taken with a Beckman DU spectrophotometer between 320 and 1360 mμ. Powdered samples were protected from the atmosphere by sealing them in a compartment made from a glass backing plate, rubber gasket, and sodium chloride window cemented together with Vaseline. A powdered $MgCO_3$ reference was prepared in a similar cell. All samples where handled in an inert atmosphere bag.

Results

Three complexes of acetonitrile with nickel(II) perchlorate have been isolated. Major infrared peaks are tabulated in Table I. Electronic spectra are recorded in Table II, and the magnetic measurements are given in Table III.

TABLE I
INFRARED SPECTRA (CM.$^{-1}$)[a]

	$[Ni(CH_3CN)_6](ClO_4)_2$	$[Ni(CH_3CN)_4(ClO_4)_2]$	$[Ni(CH_3CN)_2(ClO_4)_2]$
C≡N	2290 (m)	2295 (m)	2290 (m)
ClO_4^-			1195 (s)
	1082 (s, b)	1135 (s)	1106 (s)
	1035 (sh)	1012 (s)	1000 (s)
	945 (m)	945 (w)	950 (m)
		912 (s)	920 (s)

[a] s, strong; m, medium; w, weak; b, broad; sh, shoulder.

TABLE II
ELECTRONIC SPECTRA OF NICKEL(II)–ACETONITRILE COMPLEXES[a]

	$^3A_{1g} \rightarrow {}^3T_{2g}$		$^3A_{1g} \rightarrow {}^1E_g$	$^3A_{1g} \rightarrow {}^3T_{1g}(F)$		$^3A_{1g} \rightarrow {}^3T_{1g}(P)$		
Compound	Obsd.	Calcd.	Obsd.	Obsd.	Calcd.	Obsd.	Calcd.	*Dq*
$[Ni(CH_3CN)_6](ClO_4)_2(s)$	10,600		13,900	17,500	17,100	28,100	28,400	1060
CH_3CN soln.	10,400 (5.5)		13,900 (1.4)	17,200 (4.6)		27,200 (6.3)		
$[Ni(CH_3CN)_4(ClO_4)_2](s)$	. . .	9680	13,900	16,100	15,900	26,300	26,600	968
$[Ni(CH_3CN)_2(ClO_4)_2](s)$	8,750		13,700 sh	14,500	14,400	25,000	25,000	875

[a] Band positions in cm.$^{-1}$; ε values in parentheses.

The compound $[Ni(CH_3CN)_6](ClO_4)_2$, isolated as purple crystals, is prepared by dehydrating an acetonitrile solution of hydrated nickel(II) perchlorate with P_2O_5. Vigorous methods were necessary to remove the last moles of the coordinated water; the complex is extremely hygroscopic, hydrolyzing with atmospheric moisture and losing acetonitrile. The compound was considered anhydrous when there was no infrared absorption at 3500 cm.$^{-1}$. At this frequency the O–H stretching mode has a large extinction; consequently this is a sensitive test for water.

A number of other drying agents were tried in an effort to produce an anhydrous product. Dimethoxypropane did not give good results with the acetonitrile system. It is possible that the acetone and methanol produced coordinated so strongly with the nickel that they could not be displaced even with a large excess of acetonitrile. Anything basic or giving basic products removed the nickel from solution as the oxide. Other common drying agents were unsuccessful in removing the coordinated water. However, P_2O_5 was found to give good results, reacting with the water and not precipitating nickel phosphates.

The other two compounds are prepared by the loss of acetonitrile under vacuum. $[Ni(CH_3CN)_4(ClO_4)_2]$, a pale blue powder, results from the loss of 2 moles of acetonitrile at 65°. The third compound, pale green $[Ni(CH_3CN)_2(ClO_4)_2]$, can be made by the removal of an additional 2 moles of acetonitrile at 75°. Both of these compounds are extremely sensitive to water and organic solvents.

Discussion

Changes in the infrared spectrum of the compounds in the region between 1200 and 1000 cm.$^{-1}$ indicate that perchlorate enters the coordination sphere of the nickel as the acetonitrile is removed. Major peaks in the spectra of the compounds are given in Table I.

Hathaway and Underhill[8] have done extensive work on the infrared spectra of ionic perchlorate and perchlorato groups and the effect of perchlorate coordination on the infrared spectrum. As the symmetry of the perchlorate ion is reduced the spectrum changes; consequently one should be able to distinguish between ionic, monodentate, and bidentate perchlorate by means of infrared spectroscopy.

Ionic perchlorate has a regular tetrahedral structure and belongs to the point group T_d; two of its allowed vibrational modes are infrared active. One of these occurs as a very broad, strong band with a poorly defined maximum at 1110 cm.$^{-1}$. The second, at 630 cm.$^{-1}$, is beyond the range of sodium chloride instruments. At 930 cm.$^{-1}$, a very weak absorption is observed which is theoretically forbidden in the infrared.[8] In $[Ni(CH_3CN)_6](ClO_4)_2$ the perchlorate is ionic and exhibits the characteristic broad band at 1082 cm.$^{-1}$ and the weaker absorption at 945 cm.$^{-1}$.

TABLE III
MAGNETIC DATA AND CALCULATED VALUES OF B AND χ FOR NICKEL(II)–ACETONITRILE COMPLEXES

Compound	T, °K.	$\chi \times 10^6$ obsd.	μ_{eff}	B', cm.$^{-1}$	λ, cm.$^{-1}$	Dq, cm.$^{-1}$
$[Ni(CH_3CN)_6](ClO_4)_2$	295	4158	3.15	920	−218	1060
$[Ni(CH_3CN)_4(ClO_4)_2]$	297	4328	3.20	878	−255	968
$[Ni(CH_3CN)_2(ClO_4)_2]$	294	4510	3.30	884	−267	875

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(8) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

On monodentate coordination to a metal ion, the perchlorate symmetry is reduced to C_{3v}. Hathaway and Underhill demonstrated that the broad, degenerate absorption peak present with ionic perchlorate splits into two well-defined bands with maxima between 1200 and 1000 cm.$^{-1}$ when the perchlorate is coordinated in a monodentate fashion. An equally strong band appears between 940 and 890 cm.$^{-1}$. [$Ni(CH_3CN)_4(ClO_4)_2$] shows two well-resolved bands at 1135 and 1012 cm.$^{-1}$. A strong band is observed at 912 cm.$^{-1}$, and the band at 945 cm.$^{-1}$ in the ionic perchlorate has become less intense in the monodentate perchlorato species.

Perchlorate can also act as a bidentate ligand, coordinating through two of its oxygens. When this occurs the perchlorate symmetry is further lowered to C_{2v} and the original broad band of the perchlorate ion is split into three peaks in the 1200–1000 cm.$^{-1}$ region, as shown by Hathaway and Underhill's treatment. The normally forbidden band at 930 cm.$^{-1}$ in the ionic form will now absorb strongly. Three intense, well-resolved bands at 1000, 1106, and 1195 cm.$^{-1}$ are observed for [$Ni(CH_3CN)_2(ClO_4)_2$]. In addition a strong band at 920 cm.$^{-1}$ is present, as predicted.

While coordination of perchlorate as both a monodentate and a bidentate ligand has been reported for nickel(II), both modes of coordination have never been observed in the same system. This system with acetonitrile is the first observed where both mono- and bidentate perchlorate exist. Infrared data indicate that perchlorate enters the coordination sphere as a monodentate ligand in [$Ni(CH_3CN)_4(ClO_4)_2$] and as a bidentate ligand in [$Ni(CH_3CN)_2(ClO_4)_2$], displacing two and four moles, respectively, of acetonitrile. The infrared spectra of these complexes in the 1200–1000 cm.$^{-1}$ region are reproduced in Figure 1. It can immediately be seen from these spectra that each is of a discrete compound, containing very little (if any) of the other two.

Coordinated acetonitrile is characterized by a sharp peak at 2290–2295 cm.$^{-1}$ in these compounds.

A coordination number of six for the nickel is possible for each of the complexes. Electronic spectral data (Table III) support octahedral coordination for the complexes of acetonitrile with nickel(II) perchlorate. The pale colors observed in these compounds are indicative of the low intensity transitions typical of octahedral nickel(II).

Spectra of these complexes may be discussed in terms of ligand field theory. The triplet–triplet transitions are assigned to the three strongest bands in the electronic spectra. Extinction coefficients obtained for these bands from the acetonitrile solution spectrum of [$Ni(CH_3CN)_6$]$(ClO_4)_2$ are of the order of magnitude expected for this type of transition. Assigning the lowest energy band in these spectra as ν_1 we obtain Dq. Observed values of ν_2 and ν_3 then allow us to calculate B', and from B' and Dq one obtains calculated values of ν_2 and ν_3.[9]

The spectrum of [$Ni(CH_3CN)_6$]$(ClO_4)_2$ gives a value for Dq of 1060 cm.$^{-1}$. The data in Table III show good agreement between theory and experiment. [$Ni(CH_3CN)_2(ClO_4)_2$] exhibits the same characteristic absorption peaks for octahedral nickel(II) (Table III); again, assignments for [$Ni(CH_3CN)_2(ClO_4)_2$] correlate well with theory.

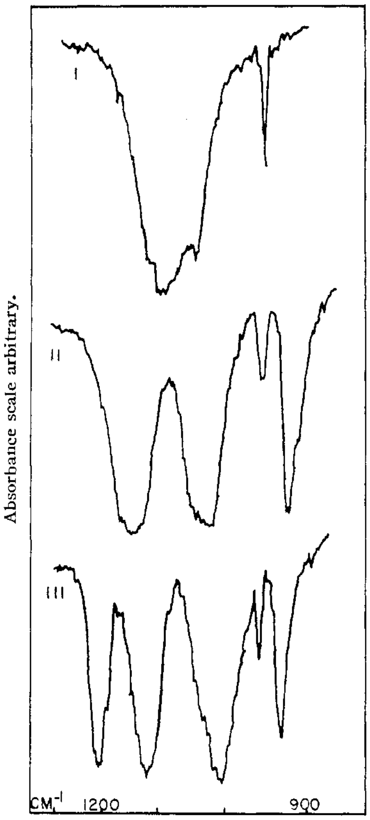

Figure 1.—Infrared spectra of the perchlorate group in the 1000 cm.$^{-1}$ region of I, [$Ni(CH_3CN)_6$]$(ClO_4)_2$; II, [$Ni(CH_3CN)_4(ClO_4)_2$]; and III, [$Ni(CH_3CN)_2(ClO_4)_2$].

The low-energy region of the electronic spectrum of [$Ni(CH_3CN)_4(ClO_4)_2$] is poorly resolved, and the first ligand field band cannot be located. However, the other three absorption bands are resolved. Applying Jørgensen's rule of average environment[9] it is possible to estimate Dq for this complex. Using the data for [$Ni(CH_3CN)_2ClO_4)_2$], Dq for perchlorate in this complex is 780 cm.$^{-1}$. We calculate a similar value, 730 cm.$^{-1}$, from data given by Hathaway, Holah, and Hudson[4] for the compound [$Ni(H_2O)_2(ClO_4)_2$], which also contains bidentate perchlorate. The similarity of these values indicates that 780 cm.$^{-1}$ is a reasonable value of Dq for perchlorate in these compounds. With this value and 1060 cm.$^{-1}$ for acetonitrile, Dq for [$Ni(CH_3CN)_4(ClO_4)_2$] is set at 968 cm.$^{-1}$. Calculated values of ν_2 and ν_3 agree with those observed experimentally.

In all three compounds a weaker band or shoulder occurs between 13,700 and 13,900 cm.$^{-1}$. From Liehr and Ballhausen's energy level diagram for octahedral nickel(II),[10] it is seen that the energy difference between the ground state and the ^1E_g level remains constant for all valves of Dq. We assign this absorption to the $^3A_{1g} \rightarrow {}^1E_g$ transition. The observed intensity is

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(9) O. Bostrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

(10) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959).

considerably larger than expected for a triplet–singlet transition; the observed absorption maxima occur at higher frequencies than predicted from Liehr and Ballhausen's diagram. However, it has been proposed that this transition may share intensity with a neighboring triplet–triplet transition and be shifted toward it.[11]

Magnetic data for these complexes are summarized in Table III. All compounds have moments falling in the range generally observed for octahedral nickel(II). From these data and Dq, it is possible to calculate values for λ, the spin–orbit coupling constant. These parameters are related by[12]

$$\chi = \frac{8N\beta^2}{3kT}\left(1 - \frac{4\lambda}{10Dq}\right)^2 + \frac{8N\beta^2}{10Dq}$$

It can be seen that λ decreases regularly in magnitude as Dq increases; all compounds have values of λ which are considerably reduced in magnitude from the free ion value of -324 cm.$^{-1}$. Diminishing absolute values of λ have been attributed to covalency.[13] In the complexes under consideration λ increases in absolute value with increasing perchlorate coordination. Certainly, one would assume perchlorato compounds to exhibit appreciable ionic character.

Reduction in B' values has also been attributed to the same cause.[13] While the B' values in these complexes are reduced from that for the free ion (1041 cm.$^{-1}$), they show a different order than do the λ values. It is possible that the B' values are not as reliable an indication of covalent character as are the λ values.

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[11] M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, **2**, 1178 (1963).

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Magnetic Investigation of Some Tetracoordinated Nickel(II) and Copper(II) Complexes between 80 and 300°K.[1]

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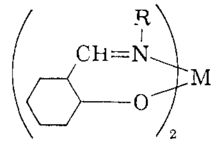
The magnetic susceptibilities between 80 and 300°K. of various N-substituted salicylaldimino complexes of nickel(II) and copper(II) have been measured. The susceptibilities of the distorted tetrahedral complexes of nickel follow the Curie–Weiss law with θ = 9–14°K. and the room-temperature magnetic moments are 3.29–3.34 B.M. The room-temperature moments of the complexes $(R_4N)_2NiX_4$ (X = Cl, Br, I; R = C_2H_5, n-C_3H_7), 3.44–3.89 B.M., are higher and for these 30°K. $> \theta >$ 8°K. Some N-aryl salicylaldiminonickel(II) complexes which are probably polymeric with the octahedral structure have room temperature magnetic moments of 3.33–3.39 B.M. and -11°K. $> \theta > -16$°K. The susceptibilities of all copper(II) complexes examined follow the Curie law. The moments of the distorted tetrahedral N-*sec*-alkylsalicylaldiminocopper complexes are slightly larger than those of the N-*n*-alkyl-substituted planar isomers, being 1.90–1.92 and 1.85–1.86 B.M., respectively. The moments of the pseudo-tetrahedral compounds $((C_2H_5)_4N)_2CuX_4$ (X = Cl, Br) are 1.93–1.97 B.M.

Introduction

While it was shown that the complexes of the type



(M = Ni(II), Cu(II); R = alkyl, aryl; the complexes are written simply as M–Sal–R). Ni–Sal–*n*-alkyl and Cu–Sal–*n*-alkyl, have a square-planar coordination structure,[2,3] the isomeric compounds Ni(Cu)–Sal–*sec*-alkyl provided us with the first known examples of chelate compounds of nickel(II) and copper(II) that have a tetrahedral coordination structure.[4–8] The angle between the planes of the chelate rings, which indicates deviations from the regular tetrahedral structure, is 81° for Ni–Sal–isopropyl[8] and 60° for Cu–Sal–isopropyl.[9] It therefore appeared interesting to compare the magnetic properties of these complexes with those of the less distorted tetrahedral halo complexes of the same metals, and, for copper, with those of the square-planar isomers. The results are to be compared with the theoretical predictions of Figgis.[10,11]

[1] This work was supported by the U. S. Department of the Army through its European Research Office, under Contract No. DA-91-591-EUC-2965, and by the Italian "Consiglio Nazionale delle Ricerche."

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