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Theoretical and experimental studies of IR spectra of 4-aminopyridine metal(II) complexes

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Abstract

In this study FT-IR spectra of $M(L)_2Ni(CN)_4$ {where M = Fe or Zn, L = 4-aminopyridine} complexes are reported for the first time in the 400–4000 cm^{-1} range. The spectral features suggest that the compounds are similar in structure to the Hofmann-type complexes with infinite polymeric layers formed with $Ni(CN)_4^{-2}$ ions bridged by $M(L)_2^{+2}$ cations. IR frequency shifts, upon formation of coordination compound are reliable indicators of the coordination mode of 4-aminopyridine. It is concluded that the ring nitrogen and not the amino nitrogen is involved in complex formation. In order to investigate metal–ligand coupling peculiarities, the vibrational wavenumbers of free and coordinated 4-aminopyridine have been calculated by a force field refinement method. The results indicated that the force field of free 4-aminopyridine should be altered in complex formation in order to represent the experimental data.

Keywords: Aminopyridine; Tetracyanonickelate complexes; Normal coordinate analysis; Force field refinement; IR spectrum

1. Introduction

4-aminopyridine is a potassium channel blocker and it is widely used in pharmacological and medical applications [1–3]. Moreover aminopyridines are immensely used in analytical chemistry as reagents. In a recent paper we reported the IR spectra of transition metal tetracyanonickelate complexes of 4-aminopyridine, $M(4Apy)_2Ni(CN)_4$ {where M = Mn, Co, Ni, Cu or Cd; 4Apy = 4-aminopyridine} [4], and it was shown that several modes of 4Apy had upward shifts in frequency compared with those of the free molecule and the shifts were metal-dependent. In order to investigate the coordination effects on 4Apy in this study we have performed normal coordinate analysis on free and coordinated 4Apy. On the other hand, we have also prepared two new compounds of 4Apy. In this paper we report the IR spectra of Fe(II) and Zn(II) tetracyanonickelate complexes of 4-aminopyridine, $M(4Apy)_2Ni(CN)_4$ {where M = Fe or Zn, abbreviated here after as M–Ni–4Apy} for the first time. The aim of this study is to investigate the coordination affects on 4Apy ligand both experimental and theoretical methods.

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2. Experimental and theoretical methods

All the chemicals used were reagent grade (Merck). The complexes were prepared using the method given in Ref. [5]. The C, H, N analysis results for the investigated complexes are: *Anal. Found* for Fe–Ni–4Apy: C; 26.31%, H; 1.55%, N;20.49%, *Calcd.* for $Fe(4Apy)_2Ni(CN)_4$: C; 26.55%, H; 1.49%, N; 20.65%, *Anal. Found* for Zn–Ni–4Apy: C; 26.17%, H; 1.50%, N; 20.30%, *Calcd.* for $Zn(4Apy)_2Ni(CN)_4$: C; 25.94%, H; 1.45%, N; 20.18%.

The IR spectra of nujol mulls or KBr discs were recorded on a Jasco 300E FT-IR spectrometer (2 cm^{-1} resolution).

For theoretical calculations, program LEV [6] was used. The methods implemented in the program were described in detail in Ref. [7]. The quantum-optimised geometry was obtained by AM1. We first carried out normal coordinate analysis on free 4Apy, in order to obtain reliable force field of the molecule. Force constants were obtained by the refinement of corresponding force constants of pyridine molecule, which were calculated by the refinement of benzene force constants in our previous work [7]. We then performed our calculations on a model of coordinated 4Apy in two steps. In the first step of the calculation, the defined parameter sets of the force field of free 4Apy were used without any modification, only force constants related to M–N(4Apy) bond were introduced. At this first step we investigated kinematic coupling of M–N bond vibrations with those of 4Apy vibrations. At the second step of calculation the ring force constants were refined, in order to produce the experimental shifts. (4Apy) N–M bond distance was set at 2.0 Å.

3. Results and discussion

3.1. $M(4Apy)_2Ni(CN)_4$ complexes

The FT-IR spectrum of the Fe–Ni–4Apy is given in Fig. 1. The IR spectra of the Fe–Ni–4Apy and Zn–Ni–4Apy complexes are found to be very similar indicating that they have similar structures.

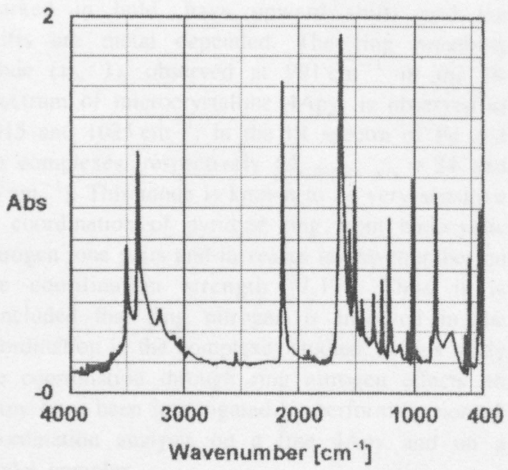

Fig. 1. The FT-IR spectrum of the Fe–Ni–4Apy.

Table 1
The wavenumbers (cm^{-1}) of 4Apy in M–Ni–4Apy complexes

Assignment [8]	4Apy		M–Ni–4Apy	
	[8]	This study	Fe	Zn
$\nu_a(NH_2)$	3433	3434vs	3515s	3435vs
$\nu_s(NH_2)$	3302	3300vs	3417vs	3358vs
νCH		3093m	3096vw	–
νCH		3073m	3066vw	3070vw
νCH		3058w	3041vw	3042vw
νCH	3038	3034m	3020vw	–
$\delta(NH_2)$	1645	1648vs	1638vs	1638vs
ν_{ring}, ν_4, 8a	1596	1602vs	**1610s**	**1621s**
ν_{ring}, ν_{13}, 8b	1555	1556s	**1561m**	**1562s**
ν_{ring}, ν_5, 19a	1508	1506s	**1517s**	**1524s**
ν_{ring}, ν_{14}, 19b	1435	1440w	**1455m, 1445sh**	**1466m**
ν_{ring}, ν_{15}, 14	1334	1333s	**1353s**	**1364s**
$\nu(C-NH_2)$, ν_3, 13	1270	1268s	1279s	1294s
δ CH, ν_6, 9a	1219	1215vs	1217vs	1218vs
δ_{ring}, ν_7, 18a	1052	1055m	1055m	1058s
Ring breath, ν_9, 1	990	991s	**1015vs**	**1025vs**
γ_{CH}, ν_{20}, 17a		950sh	950vw	961vw
γ_{CH}, ν_{21}, 10a		884sh	882vw	882vw
X-sens., ν_8, 12	842	842m	**852m**	**857m**
γ_{CH}, ν_{23}, 5	824	822s	813vs	828vs
γ_{ring}, ν_{25}, 4	680	680m	727vw	728vw
δ_{ring}, ν_{19}, 6b		661m	670vw	677vw
X-sens., ν_{10}, 6a		536s	**557s**	**575s**
X-sens., ν_{26}, 11		522sh	522vs	527vs
γ_{ring}, ν_{22}, 16a		408m	420sh	423m

Coordination sensitive wavenumbers are marked as bold.

Table 2
The wavenumbers (cm^{-1}) of the $Ni(CN)_4$ vibrations of the M–Ni–4Apy complexes

Assignment	Fe	Zn	Cd–Ni–Py[a]	Zn–Ni–py[a]	Rel. int.
E_u ν(CN)	2146	2164	2154	2165	vs
$\nu(^{13}CN)$	2108	2131	2111	2124	vw
E_u ν(NiC)	552	–	543	547	m
A_{2u} π(NiCN)	447	450	–	449	sh
E_u δ(NiCN)	430	436	425	431	vs

[a] $M(pyridine)_2Ni(CN)_4$ complexes (M = Cd or Zn) taken from Ref. [11].

The wavenumber of Fe–Ni–4Apy and Zn–Ni–4Apy complexes are tabulated in Table 1 together with those of polycrystalline 4Apy [8].

4Apy has two nitrogen atoms, each having a lone pair electrons to donate. IR spectroscopy is diagnostic for the coordination mode of 4-amino-pyridine. It is well known that when amino nitrogen atom are involved in coordination a drastic red shift observed in NH_2 stretching vibrations ($\Delta = 150 - 200\,cm^{-1}$) [9–10]. Since we do not observe any important red shift in NH_2 stretching vibrations, we conclude that amino group nitrogen of 2Apy does not involve in coordination. On the other hand certain modes of 4Apy, which are marked in bold, have upward shifts and the shifts are metal depended. The ring breathing mode (ν_9, 1), observed at $991\,cm^{-1}$ in the IR spectrum of microcrystalline 4Apy, is observed at 1015 and $1025\,cm^{-1}$, in the IR spectra of Fe and Zn complexes, respectively ($\Delta_{complex-cry} = 24$ and $34\,cm^{-1}$). This mode is known to be very sensitive to coordination of pyridine ring from endocyclic nitrogen lone pairs and increases in wavenumber on the coordination strength [7,11]. Thus it is concluded that ring nitrogen is involved in the coordination in the complexes studied. In this study the coordination through ring nitrogen effects on 4Apy have been investigated by performing normal coordination analysis on a free 4Apy and on a model complex.

The vibrational wavenumbers of the $Ni(CN)_4$ group for the complexes studied are given in Table 2 together with those of Hofmann type pyridine complexes [11] for comparison. The characteristic wavenumbers of the ν(CN) and δ(NiCN) modes are found to be similar to those of Hofmann type clathrates [12] and pyridine complexes [11], indicating that they have analogous structures with two dimensional networks in which M takes an octahedral coordination with a pair of 4Apy ligands protruding above and below

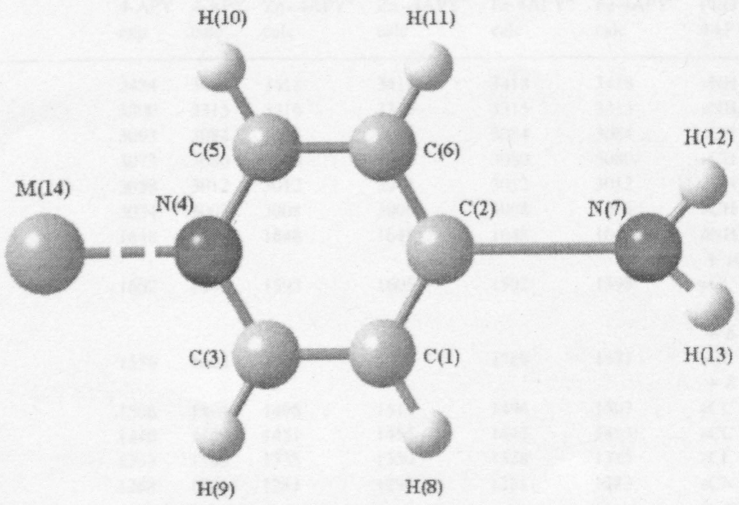

Fig. 2. Atom numbering of M–4APY (M = Zn or Fe).

Table 3
The definitions of normal vibrational coordinates and geometrical parameters of M–4APY (M = Fe or Zn)

	Type	Value (Å/°)	Atoms		Type	Value (Å/°)	Atoms
1	Bond	1.41740	C1–C2	26	Angle	115.590	N4–C5–H10
2	Bond	1.40057	C3–C1	27	Angle	119.031	C5–N4–M14
3	Bond	1.34732	N4–C3	28	Angle	118.733	C5–C5–C2
4	Bond	1.34740	N4–C5	29	Angle	120.180	C6–C5–H10
5	Bond	1.40062	C5–C6	30	Angle	120.083	C5–C6–H11
6	Bond	1.41729	C6–C2	31	Angle	121.280	C6–C2–N7
7	Bond	1.38905	C2–N7	32	Angle	121.173	C2–C6–H11
8	Bond	1.09720	C1N8	33	Angle	115.788	C2–N7–H12
9	Bond	1.10534	C3–H9	34	Angle	115.793	C2–N7–H13
10	Bond	1.10538	C5–H10	35	Angle	114.841	H12–N7–H13
11	Bond	1.09718	C6–H11	36	O.p. bend	3.105	C6–C2–C1–N7–C2–N7
12	Bond	0.99353	N7–H12	37	O.p. bend	0.758	C3–C1–C2–H8–C1–H8
13	Bond	0.99344	N7–H13	38	O.p. bend	0.682	C1–C3–N4–H9–C3–H9
14	Bond	2.00000	N4–M14	39	O.p. bend	0.742	N4–C51–C6–H10–C5–H10
15	Angle	118.728	C2–C1–C3	40	O.p. bend	0.809	C2–C6–C5–H11–C6–H11
16	Angle	117.337	C1–C2–C6	41	Torsion	179.178	C6–C2–C1–C2–C1–C3
17	Angle	121.168	C1–C2–N7	42	Torsion	179.524	C2–C1–C3–C1–C3–N4
18	Angle	121.168	C2–C1–H8	43	Torsion	179.879	C1–C3–N4–C3–N4–C5
19	Angle	124.236	C1–C3–N4	44	Torsion	179.842	C3–N4–C5–N4–C5–C6
20	Angle	120.101	C3–C1–H8	45	Torsion	179.454	N4–C5–C6–C5–C6–C2
21	Angle	120.179	C1–C3–H9	46	Torsion	179.146	C5–C6–C2–C6–C2–C1
22	Angle	116.731	C3–N4–C5	47	Torsion	157.486	C6–C2–N7–C2–N7–H12
23	Angle	115.584	N4–C3–H9	48	Torsion	157.488	C1–C2–N7–C2–N7–H13
24	Angle	119.014	C3–N4–M14	49	Torsion	22.331	C3–N4–C5–M14–N4–M14
25	Angle	124.229	N4–C5–C6				

Table 4
The calculated wavenumbers (cm^{-1}) of free and coordinated 4-APY

Assignment	4-APY exp	4-APY calc	Zn–4APY[a] calc	Zn–4APY[b] calc	Fe-4APY[a] calc	Fe-4APY[b] calc	PED (%) for 4APY
NH_2 stretching (ν_{NH_2})	3434	3418	3418	3418	3418	3418	νNH_2 (99)
NH_2 stretching (ν_{NH_2})	3300	3315	3316	3316	3315	3315	νNH_2 (99)
CH stretching (ν_{CH})	3093	3084	3084	3084	3084	3084	νCH (99)
CH stretching (ν_{CH})	3073	3080	3080	3080	3080	3080	νCH (99)
CH stretching (ν_{CH})	3058	3012	3012	3012	3012	3012	νCH (99)
CH stretching (ν_{CH})	3034	3008	3008	3008	3008	3008	νCH (99)
NH_2 scissoring (δ_{NH_2})	1648	1648	1648	1648	1648	1648	δNH_2 (70) + δCNH (22) + νCN (8)
CC stretching (ν_{CC})	1602	1593	1593	1605	1592	1598	νCC (54) + δCH (20) + νCN (9) + δ ring (9)
CC stretching (ν_{CC})	1556	1568	1569	1575	1568	1571	νCC (74) + δCH (10) + δ ring (6)
CC stretching (ν_{CC})	1506	1495	1496	1511	1494	1507	νCC (78) + δCH (14)
CC stretching (ν_{CC})	1440	1449	1451	1454	1447	1453	νCC (54) + δCH (36)
CC stretching (ν_{CC})	1333	1330	1335	1350	1328	1345	νCC (43) + δCH (41)
C–NH_2 stretching (ν_{C-NH_2})	1268	1281	1283	1295	1281	1282	νCN (40) + δ ring (22) + δCH (18) + νCC (8)

Table 4 (*continued*)

Assignment	4-APY exp	4-APY calc	Zn–4APY[a] calc	Zn–4APY[b] calc	Fe-4APY[a] calc	Fe-4APY[b] calc	PED (%) for 4APY
CH i.p. bending (δ_{CH})	1215	1204	1210	1229	1213	1213	δCH (79) + νCC (16)
CH i.p. bending (δ_{CH})	–	1167	1168	1161	1166	1162	δCH (76) + δ ring (12)
CH i.p. bending (δ_{CH})	–	1110	1114	1092	1109	1110	δCH (49) + νCC (44)
CH o.p. bending (γ_{CH})	–	1053	1049	1018	1053	1054	γCH (95)
Ring deformation (δ_{ring})	1055	1055	1065	1065	1058	1048	νCC (37) + δ ring (41) + δCH (8)
Ring breathing	991	985	992	1001	989	991	νCC (54) + δCH (37)
CH o.p. bending (γ_{CH})	950	949	950	986	949	949	γCH (85) + γCN (6)
NH_2 twist	–	943	944	943	943	943	NH_2 twist (91)
CH o.p. bending (γ_{CH})	884	877	877	864	876	877	γCH (99)
ν_{C-NH_2} + δring + ν_{CC}	842	851	856	858	851	856	νCC (22) + δ ring (22) + νCN (19) + γCH (19)
CH o.p. bending (γ_{CH})	822	834	841	839	836	834	γCH (62) + γCN (10)
O.p. ring deform. (γ_{ring})	680	693	677	747	637	741	γCH (51) + γ ring (38)
NH_2wag	–	651	668	661	668	660	NH_2 wag (38) + NH_2 rock (14) + γCN (10) + δNH_2 (10)
Ring deformation (δ_{ring})	661	656	658	665	656	657	δ ring (67) + νCC (16) + δCH (12)
ν_{C-NH2} + δ_{ring} + ν_{CC} + δ_{CN}	536	537	563	563	555	548	δ ring (35) + νCN (20) + γCN (20)
γ_{CN} + γ_{ring} + δ_{ring} + NH_2 rocking	522	520	531	525	530	521	γCN (21) + γ ring (17) + NH_2 rock (17) + δ ring (25)
O.p. ring deform. (γ_{ring})	408	405	376	417	405	417	γ ring (50) + γCH (22) + δCN (6)
C–NH_2 i.p. bending (δ_{CN})	–	386	400	390	386	391	δCN (75) + νCC (16) + γ ring (6)
NH_2 rocking	–	260	261	263	259	262	NH_2 rock (94)
γ_{CN} + γ_{ring} + γ_{CH}	–	213	241	247	229	227	γCN (47) + γCH (25) + γ ring (24)
N–M stretching	–	–	194	198	184	185	–
δCNM	–	–	142	185	61	183	–
γ_{NM} + δ_{CNM} + γ_{ring} + γ_{CH}	–	–	47	49	31	46	–

[a] The wavenumbers of M–4APY calculated by using the same force constants of free 4-APY (only force constants related to M–N(4Apy) bond were introduced).

[b] The wavenumbers of M–4APY, calculated by the refined force field.

the network; the $Ni(CN)_4$ square plate shares the vertices with four octahedra to build up the 2D-network [13].

3.2. Normal coordinate analysis

The atomic numbering scheme of 4Apy is illustrated in Fig. 2. The definition of the natural vibrational coordinates and the geometrical parameters of 4Apy are tabulated in Table 3. The results of normal coordinate analysis for free and coordinated 4Apy are given in Table 4. The force constants are given in Table 5. The assignment was established depending on the experimental results [8]. The approximate description of modes, established by analysis of PED together with the atomic displacements for free 4Apy agrees well with the experimental assignment

The two steps of calculation results of the model complex of 4Apy with Fe and Zn are presented in

Table 5
Force constants of 4-Apy. Force constants of coordinated 4-Apy, that are altered from corresponding values of free 4Apy are marked as bold and the differences from the original values, $\Delta = f_{comp} - f_{free}(\Delta_{Zn}; \Delta_{Fe})$ are given in parenthesis, the rest have the same values as free molecule has bond–bond, bond–angle and angle–angle force constants are in mdyne $Å^{-1}$, mdyne Å, respectively

Type	Force constants	Type	Force constants	Type	Force constants
1–1, 6–6	6.794	7–17, 7–31	0.140	**19–21, 25–29**	**0.007 (− 0003; 0)**
2–2, 5–5	6.525	7–33, 7–34	0.164	19–22, 22–25	−0.061
3–3, 4–4	6.737	8–15, 11–28, 9–19, 10–25	0.147	**20–21, 29–30**	**0.061 (− 0.031; 0)**
2–7	5.711	8–18, 11–32, 8–20, 11–30, 9–21, 10–29	0.074	**21–22, 22–29**	**0.083 (0.038; 0)**
8–8, 11–11	5.512			**22–23, 22–26**	**− 0.111 (0.011; 0.007)**
9–9, 10–10	5.256	9–23, 10–26	0.059	38–38, 39–39	0.508
12–12, 13–13	6.740	12–33, 12–34	−0.014	37–37, 40–40	0.531
5–6, 1–2	0.628	12–35	0.063	**37–38, 39–40**	**0.076 (− 0.070; 0)**
1–6	0.769	15–15, 16–16, 28–28	1.211	37–41, 37–42, 38–42, 40–46	0.145
1–7, 6–7	0.577	**19–19, 25–25**	**1.211 (0.041; 0)**	**39–45, 40–45**	**0.145 (− 0.009; 0)**
1–8, 7–12, 2–8, 7–12, 7–13, 3–9, 4–10, 6–11, 5–11, 2–9, 5–10	0.224	17–17, 31–31	0.826	38–39, 42–45	0.038
		18–18, 32–32, 30–30, 20–20	0.510	36–36	0.487
		22–22	1.246	**37–40**	**− 0.004 (0.034; 0)**
3–4	0.641	**23–23, 26–26**	**0.498 (0.005; −0.011)**	36–42, 36–45, 40–41, 37–46, 37–43, 40–44, 38–44, 39–43	0.069
12–13	0.003	33–33, 34–34	0.495		
2–3, 4–5	**0.749 (− 0.044; − 0.044)**	35–35	0.609		
1–15, 6–28, 1–16, 6–16	0.255	21–21, 29–29	0.487	38–43, 39–44	0.164
1–17, 6–31	0.028	15–16, 16–28, 41–44, 43–46	−0.069	36–43, 37–45, 37–44, 38–45, 38–46, 40–42, 36–44, 40–42, 39–41	−0.021
1–18, 6–32	0.021	15–17, 28–31, 16–18, 16–32	−0.004		
1–20, 6–30, 7–35	−0.021	15–18, 28–32	0.011		
1–31, 6–17	−0.028	**19–23, 25–26**	**0.011 (− 0.003; 0.008)**	36–37, 36–40	0.072
3–21, 4–29	**− 0.028 (− 0.010; 0)**	15–19, 25–28	−0.072	36–38, 36–39	−0.023

Table 5 (*continued*)

Type	Force constants	Type	Force constants	Type	Force constants
2–15, 5–28	0.261	15–20, 28–30, 18–19, 25–32	0.019	36–41, 36–46	0.096
2–18, 5–32	**− 0.098 (− 0.029; 0)**	15–21, 28–29, 16–33	−0.034	41–43, 44–46, 41–45, 42–46,	0.007
2–19, 5–25	**0.212 (0; − 0.073)**	15–23, 26–28, 16–18, 31–32	0.045		
2–20, 5–30	**0.098 (− 0.029; 0)**	15–31, 17–28, 16–17, 16–20, 16–30, 42–44, 43–45, 47–48	0.004	41–46	0.114
2–21, 5–29	**0.112 (− 0.056; − 0.056)**			**43–44**	**0.138 (− 0.054; 0)**
2–23, 5–26	**− 0.070 (− 0.014; − 0.011)**	16–31, 31–34	0.049	42–42, 45–45	0.182
3–19, 4–25	0.258	16–33, 31–33	0.034	41–42, 45–46	0.130
3–22, 4–22	0.267	18–20, 30–32	−0.030	**42–43, 44–45**	**0.092 (0.014; 0)**
3–23, 4–26	**0.031 (0.014; 0.014)**	**21–23, 26–29**	**− 0.030 (− 0.007; 0)**	41–41, 46–46	0.153
7–16	−0.126	19–20, 25–30	−0.011	43–43, 44–44	0.157
				47–47, 48–48	0.030

Table 4. The metal-dependent wavenumber shifts observed upon coordination of the ligand (4Apy) to a transition metal (Fe or Zn) are found to improve after refinement of the 4Apy ring force field. Thus the calculated results on coordinated 4Apy indicates that the vibrational wavenumber shifts, observed on coordination of 4Apy to a transition metal(II) are not caused only by kinematic coupling effect but also by alterations of the ring force field.

4. Conclusions

In this study IR spectra of two new tetracyanonickelate complexes of 4Apy were presented and in order to investigate metal-dependent blue shifts observed upon coordination with respect to free molecule, a normal coordinate analysis were performed. The calculation results on coordinated 4Apy indicate that both kinematic coupling and alterations of the ring force field cause the vibrational wavenumber shift, observed on coordination.

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