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Further Characterization of Some Metal Perchlorate Complexes with Organophosphoryl Ligands

N. M. KARAYANNIS, C. M. MIKULSKI, M. J. STROCKO, L. L. PYTLEWSKI
and M. M. LABES
Department of Chemistry, Drexel University, Philadelphia, Pa., U.S.A.

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Supplementary characterization studies of some phosphonate and phosphate ester metal complexes and $Fe(TPPO)_4(ClO_4)_3$ (TPPO = triphenylphosphine oxide) led to the following conclusions. $M(DIMP)_4(ClO_4)_2$ (DIMP = diisopropyl methylphosphonate) complexes involves coordinated perchlorate and were formulated as $[M(DIMP)_4(OClO_3)](ClO_4)$. Dimethyl methylphosphonate (DMMP) complexes of the above type and $Fe(TPPO)_4(ClO_4)_3$ dot not exhibit any evidence favoring the presence of coordinated perchlorate. For these compounds the presence of a bi- or poly-nuclear complex cation of the type $[ML_4]_n^{x+}$, involving both terminal and bridging ligand groups and coordination number five for the metal ions, is proposed. Far infrared studies of the above complexes and a number of $[ML_5](ClO_4)_2$, $[ML_6](ClO_4)_{2,3}$ and $[ML_4(H_2O)_2](ClO_4)_2$ complexes with DMMP and trimethyl phosphate and tentative assignments of ν_{M-O} are also reported.

Introduction

Bulky monodentate oxo-ligands, such as phosphine oxides, arsine oxides, phosphonate esters, aliphatic amine oxides and 2- or 2,6-substituted pyridine N-oxides, form complexes of the type $M(L)_4X_2$ (X = ClO_4, ReO_4, BF_4) with divalent metal ions.[1–15] In several cases the formation of $[ML_4]^{2+}$ complexes of tetrahedral (L = hexamethylphosphoramide (HMPA); M = Mn, Fe, Co, Ni, Zn;[8] L = trimethylamine oxide (TMNO), M = Co, Ni;[9] L = tri-n-butylphosphine oxide (TBPO), M = Mn, Co, Ni, Zn;[13] L = trimethyl-, triethyl- or triphenyl-phosphine oxide (TMPO, TEPO and TPPO, respectively), triphenylarsine oxide (TPAsO), M = Co, Zn[1–3,15]) or square planar (L = 2,6-lutidine N-oxide (LNO), M = Fe, Co, Ni, Cu[11]) ligand-field symmetry was reported. In other cases, however, the spectral and magnetic properties of the $M(L)_4X_2$ complexes rule out any of the above configurations.[1–7,10,12,14] TPPO complexes of this type with Mn^{II} and Ni^{II} have been formulated as $[M(TPPO)_4]^{2+}$ and assigned a ligand-field symmetry intermediate between tetrahedral and square planar (D_{2d}).[1] The same assignment was made for the corresponding TPAsO[3] and neutral phosphonate ester[7] complexes, on the basis of the similarity of their electronic spectra to those of the TPPO analogs. Diphenylmethyl-phosphine and arsine oxide (DPMPO, DPMAsO) complexes with metal perchlorates and TPPO and TPAsO complexes with metal perrhenates are of the type $[ML_4(OZO)_3]^+$ (M = Mn through Zn, Z = Cl, Re) as shown by IR studies and a crystal structure determination.[4,6] TPPO, TPAsO and TMPO complexes with divalent 3d metal perchlorates were also formulated as $[ML_4(OClO_3)]^+$, on the basis of their electronic spectra, which point to a square pyramidal configuration.[5,6] The IR spectra of these compounds do not exhibit any splitting of the ν_3 mode of ionic perchlorate, however.[5,6] It should be stressed at this point that coordination of perrhenate does not necessarily prognosticate the coordination of perchlorate in analogous systems, since the latter coordinates less readily than ReO_4^-.[16] It is also worth noting that we have isolated complexes of the types $[Fe(TPPO)_4]^{2+}$[14] and $[Fe(TBPO)_4(OClO_3)_2]$[13] during our recent studies. Finally, for paramagnetic complexes of the type $Ni(L)_4(ClO_4)_2$ (L = LNO, 2-picoline N-oxide) hexacoordinated structures involving either two coordinated monodentate perchlorate groups[12] or both terminal and bridging pyridine N-oxide groups (polynuclear cationic complex)[10] were proposed. In a recent study we support the latter assignment for these complexes and discuss the possibility of penta- and hexa- coordination for Ni^{II}.[17]

Trivalent metal perchlorates yield $M(L)_4(ClO_4)_3$ with phosphine oxides[1,13,14] and $[ML_6](ClO_4)_3$ with dimethyl methylphosphonate (DMMP)[7] and trimethyl phosphate (TMP).[18] Complexes of the former type involve two coordinated monodentate perchlorate groups, i.e. $[ML_4(OClO_3)_2]^+$ (L = TBPO, M = Cr, Fe, Ce; L = TPPO, M = Cr, In, Ce).[13,14]

In view of the different structural possibilities discussed above, we undertook additional charakterization studies of the diisopropyl methylphosphonate (DIMP), DMMP[7] and TMP[18] complexes with metal perchlorates recently reported and of $Fe(TPPO)_4(ClO_4)_3$.[1] These studies are reported in the present paper.

Experimental Section

DIMP, DMMP and TMP complexes and $Fe(TPPO)_4(ClO_4)_3$ were prepared by procedures previously described.[1,7,18] IR spectra were obtained on Nujol mulls between IRTRAN 2 (zinc sulfide) (4000–700 cm^{-1}) and polyethylene (700–200 cm^{-1}) windows on a Perkin-Elmer 621 spectrophotometer. Nujol mull electronic spectra were obtained on a Cary 14 spectrophotometer. The complexes were allowed to stand over $CaCl_2$ in an evacuated desiccator for several weeks before spectral measurements were effected. The absence of water in most of these compounds was confirmed by IR spectroscopy (4000–1000 cm^{-1}. Only $[M(DMMP)_4(H_2O)_2](ClO_4)_2$ (M = Co, Zn) contain coordinated aquo groups, which are not removed by vacuum desiccation, as already reported.[7]

Results and Discussion

IR data for the complexes examined are given in Table I and Figures 1 and 2, together with similar data previously reported. Assignments of ν_{M-O} bands are tentative. The solid state electronic spectra of these compounds are given in Table II and Figure 3. The drying procedure described in the experimental section led to the effective dehydration of most of the complexes examined, including $[Ni(TMP)_5(H_2O)](ClO_4)_2$,[18] which yielded the corresponding water-free complex. Only $[M(DMMP)_4(H_2O)_2](ClO_4)_2$ (M = Co, Zn)[7] were not dehydrated under these conditions.

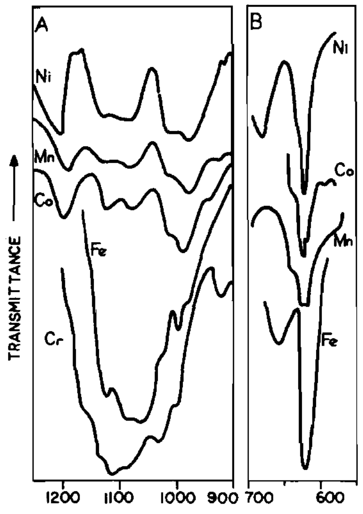

Figure 1. (A) Infrared spectra (1250–900 cm^{-1}) of $Fe(TPPO)_4(ClO_4)_3$, $[Cr_3(TPPO)_8(OClO_3)_3](ClO_4)_6$ and $M(DIMP)_4(ClO_4)_2$ (M = Mn, Co, Ni). (B) Infrared spectra (700–550 cm^{-1}) of $Fe(TPPO)_4(ClO_4)_3$, $M(DIMP)_4(ClO_4)_2$ (M = Mn, Co) and $Ni(DMMP)_4(ClO_4)_2$.

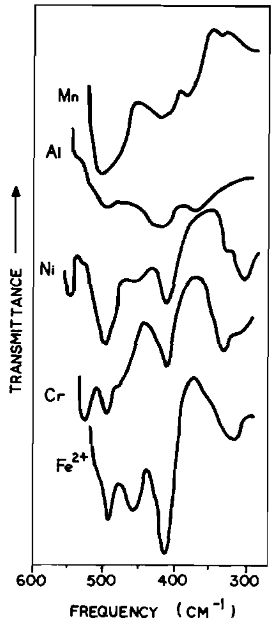

Figure 2. Far infrared spectra of $[M(DMMP)_6](ClO_4)_3$ (M = Al, Cr), $Fe(DMMP)_5(ClO_4)_2$, $Ni(DMMP)_4(ClO_4)_2$ and $Mn(DIMP)_4(ClO_4)_2$.

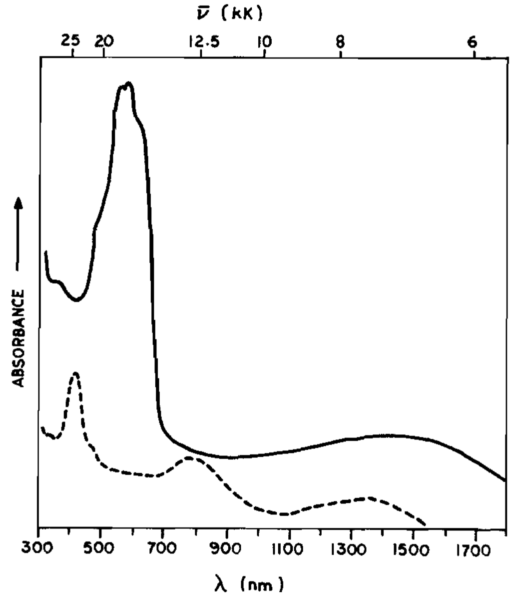

Figure 3. Solid state (Nujol mull) electronic spectra of (——) $Co(DIMP)_4(ClO_4)_2$ and (----) $Ni(DIMP)_4(ClO_4)_2$.

TABLE I. Pertinent Infrared Data for Metal Perchlorate Complexes with Organophosphoryl Ligands (cm^{-1})[a]

Compound	$\nu_{P=O}$	Ionic ClO_4^-	Coordinated $-OClO_3$	ν_{M-O}		ν_{Ligand}
				M–Ligand	M–$OClO_3$	(600–280 cm^{-1})
DIMP	1241					(580), 552, (511), 502, (496), 420b, (393), 338
$[Mn(DIMP)_4(OClO_3)](ClO_4)$	1189	1085 622	1122, (922), (635), 614	370	–	(570), 545, 508b, 416, (395), 340
$[Fe(DIMP)_4(OClO_3)](ClO_4)$	1180	1079 620	1125, (928), (640), 608	373	–	(575), 544, 504b, 413, (392), 337
$[Co(DIMP)_4(OClO_3)](ClO_4)$	1192	1082 623	1122, (930), (633), 614	375	–	(580), 542, (512), 504, (490), 420, (343)
$[Ni(DIMP)_4(OClO_3)](ClO_4)$	1197	1088 616b	1121, (930), 616b	378	–	548, 510b, (490), 420, (393), 335
$[Cu(DIMP)_4(OClO_3)](ClO_4)$	1188 1167	1090 616	–	376	–	542, 509b, (490), 420, (397), 338
$[Cd(DIMP)_4(OClO_3)](ClO_4)$	1185	1075 623	1130, (921), 623 (?)	346	–	(580), 552, (511), 506, (448), 420, (398)
$[Sr(DIMP)_4(OClO_3)](ClO_4)$	1210	1099 620b	1132, (935), 620b	341	–	(575), 540, 498b, 415, (392)
DMMP	1247					566, (538), 496, 463, (419), 410, (393), (334), 300b
$[Al(DMMP)_6](ClO_4)_3$	1212	1080 621	–	369	–	(575), 540, 500, (470), 418, 300b
$[Cr(DMMP)_6](ClO_4)_3$	1181	1085 623	–	349	–	(566), 534, 490, 467, 423, (325), 293
$[Mn(DMMP)_6](ClO_4)_2$	1203	1085 618	–	280	–	556, 495, (460), 410, 304
$[Fe(DMMP)_5](ClO_4)_2$	1181	1085 622	–	320	–	(570), 497, 464, 416, (305)
$[Fe(DMMP)_6](ClO_4)_3$	1162	1081 623	–	326b	–	(575), 500, 458, 419, (301)
$[Co(DMMP)_4(H_2O)_2](ClO_4)_2$	1208	1091 620	–	?	–	498, (468), 411 (336), 308
$[Ni(DMMP)_4]_n(ClO)_4)_{2n}$	1211	1100 621	–	(324)	–	552, 498, (460), 412, 308
$[Cu(DMMP)_4]_n(ClO_4)_{2n}$	1202	1102 624	–	328	–	(570), 530, 495, 475, 409, 304
$[Zn(DMMP)_4(H_2O)_2](ClO_4)_2$	1166	1099 616	–	?	–	(530), 492, (470), (420), 406, (328), 304
TMP	1278					568, (535), (505), 488, 444, 360, 300b
$[Mg(TMP)_6](ClO_4)_2$	1255	1085 621	–	348	–	542, 500b, 452, 369b, 302b
$[Cr(TMP)_6](ClO_4)_3$	1213	1078 620	–	388	–	552, (535), 488, 450, (368), 304
$[Mn(TMP)_5](ClO_4)_2$	1238	1070 619	–	(354)	–	(550), 500b, 448, 362, (300)
$[Fe(TMP)_5](ClO_4)_2$	1239	1080 620	–	360	–	549, (504), 492, 446, (368), 304
$[Fe(TMP)_6](ClO_4)_3$	1202	1075 618	–	376	–	541, 490, 452, 370, (302)
$[Co(TMP)_5](ClO_4)_2$	1230	1085 622	–	377	–	(554), 505b, 455 368, 310b

TABLE I. (Cont.)

Compound	$\nu_{P=O}$	Ionic ClO_4^-	Coordinated $-OClO_3$	ν_{M-O}		ν_{Ligand} (600–280 cm^{-1})
				M–Ligand	M–$OClO_3$	
$[Ni(TMP)_5](ClO_4)_2$	1236	1077 621	–	379	–	(551), 523, 497, 457, (388), 370, (295)
$[Cu(TMP)_5](ClO_4)_2$	1222	1065 620	–	(382)	–	(542), (510), 496, 455, 372, 300b
$[Zn(TMP)_5](ClO_4)_2$	1226	1070 619	–	(350)	–	557, (538), 500b 460, 370
TPPO	1195				–	545, 507, 460, 451, 403, 293
$[Mg(TPPO)_4]_n(ClO_4)_{2n}$	1180	1090 622	–	432 348	–	540, (520), (455), 440, 306
$[Cr(TPPO)_4(OClO_3)_2](ClO_4)$	1136 1118	1070 620	1150, 1020, 920, 655, 615, 490	442	340	538, 411, (395), 305
$[Cr_3(TPPO)_8(OClO_3)_3](ClO_4)_6$	1116	1080 622	1155, 1030, 918, 648, 612, 485	455 380	312	540, (442), 420
$[Fe(TPPO)_4]_n(ClO_4)_{3n}$	1118	1077 621	–	429 344	–	540, 530, (507), 475, (420), (391), 298
$[Co(TPPO)_4](ClO_4)_2$	1146	1088 622	–	426	–	538, (528), (490), 440, (395), 315b
$[Ni(TPPO)_4]_n(ClO_4)_{2n}$	1170 1145	1094 619	–	429 350	–	539, (528), 510, (495), 475, 410, 390, 295

[a] IR data (4000–700 cm^{-1}) for DIMP, DMMP and TMP complexes from refs. 7 and 18; low-frequency IR data (700–250 cm^{-1}) for the same complexes from the present work. IR spectrum (4000–700 cm^{-1}) of $Fe(TPPO)_4(ClO_4)_3$ from ref. 22; low-frequency IR spectrum (700–250 cm^{-1}) of this complex from the present work. IR data for the rest of the TPPO complexes of the Table from refs. 14, 22.
b: broad; shoulders in parentheses.

DIMP Complexes

Splitting of the ν_3 and intensification of the ν_1 mode of ionic perchlorate were previously reported for the DIMP complexes and attributed[7] to a lowering of the tetrahedral symmetry of this anion in the crystal lattice.[19] Examination of the spectra of these complexes in the region below 700 cm^{-1} shows that the ν_4 mode is also split (Table I, Fig. 1). Additional perchlorate bands may occur at ca. 1030 and below 500 cm^{-1},[20,21] but are masked by ligand absorptions in this region. The above evidence points, therefore, to the presence of coordinated perchlorate[20,21] rather than lowering of the site symmetry of the polyanion in the crystal lattice.[19] The solid state (Nujol mull) electronic spectra of the Co^{II} and Ni^{II} complexes (Table II, Fig. 3) may also be attributed to a pentacoordinated configuration.[4–6,18] Mull electronic spectra of these complexes were previously obtained by using filter paper as carrier of the mull, and found to be very similar to those of DIMP solutions of these compounds.[7] Better resolution of the spectra was effected during the present work, by applying the mull on a sheet of thinner paper (e.g. tissues of the commercial product "Kimwipes"). Thus, the infrared and electronic spectra of DIMP complexes suggest that these compounds are of the type $[M(DIMP)_4(OClO_3)](ClO_4)$ (M = Mg, Ca, Sr, Mn, Fe, Co, Ni, Cu, Cd)[7] in the solid state. The Cu^{II} complex does not exhibit splittings of the perchlorate bands, as is also the case with the DPMAsO analog.[6] Tentative assignments of ν_{M-O} (ligand) bands were made for the DIMP complexes (Table I, Fig. 2), but no bands attributable to ν_{M-O} (perchlorate) were identified. These bands are either very weak or overlap with ligand absorptions in complexes involving weakly coordinated perchlorate.[5,6]

DMMP, TMP and TPPO Complexes

The IR spectra of the DMMP and TMP complexes examined and $Fe(TPPO)_4(ClO_4)_3$ are generally characterized by the absence of bands attributable to coordinated perchlorate (Table I, Fig. 1).[7,18–22] The strong band at 1095 cm^{-1} in the latter complex (Fig. 1) is assigned to the free ligand absorption at 1097 cm^{-1}, which is generally intensified upon complex forma-

TABLE II. Solid-State Electronic Spectra of Some Pentacoordinated 3d Metal Complexes with Organophosphoryl Ligands.

Complex	$\bar{\nu}$, kK	Reference
$[Fe(TPPO)_4]_n(ClO_4)_{3n}$	29.0s	1
$[Co(DIMP)_4(OClO_3)](ClO_4)$	20.0sh	[a]
	17.8s	
	17.3s	
	16.4sh	
	6.5m, vb	
$[Co(TMPO)_5](ClO_4)_2$	20.2sh	5
	19.65s	
	18.4s	
	16.9s	
	10.5m	
	7.6m, b	
$[Co(TMP)_5](ClO_4)_2$	20.8s, sh	18
	19.4s	
	19.0s	
	17.1sh	
	13.9sh	
	10.8m	
	8.3–5.5m, vb	
$[Ni(DIMP)_4(OClO_3)](ClO_4)$	23.8s	[a]
	20.6sh	
	12.7m, b	
	7.35m–w, vb	
$[Ni(TMPO)_5](ClO_4)_2$	22.2s	5
	19.2sh	
	17.15w	
	13.5sh	
	11.3m	
	8.7w, b	
$[Ni(TPPO)_4]_n(ClO_4)_{2n}$	23.2	6
	20.0sh	
	17.1	
	14.1	
	11.7	
	8.0b	
$[Ni(DMMP)_4]_n(ClO_4)_{2n}$	23.2s	[a]
	20.0sh	
	12.2m, vb	
	6.7m, vb	
$[Ni(TMP)_5](ClO_4)_2$	22.6s	[a]
	19.3m, sh	
	18.5m, sh	
	15.9m, sh	
	11.9m, vb	
	7.3m, vb	
$[Cu(DIMP)_4(OClO_3)](ClO_4)$	10.65s, vb	[a]
$[Cu(TMPO)_4(OClO_3)](ClO_4)$	16.7sh	5
	11.4m, b	
$[Cu(DMMP)_4]_n(ClO_4)_{2n}$	10.7s, vb	[a]
$[Cu(TMP)_5](ClO_4)_2$	16.7w, sh	18
	11.6m, sh	
	10.7s, b	

[a] This work.

tion.[23] Weak coordination of perchlorate is this compound and the $M(DMMP)_4(ClO_4)_2$ (M = Ni, Cu) complexes is possible.[4–6] However, TBPO forms with Cr^{III} and Fe^{III} isomorphous complexes of the type $[M(TBPO)_4(OClO_3)_2](ClO_4)$ which clearly show splittings of the polyanion vibrational modes.[13] Thus, if the Fe^{III}–TPPO complex contained coordinated perchlorate it would most probably be isomorphous to $[Cr(TPPO)_4(OClO_3)_2](ClO_4)$[14] (Table I). We attempted the synthesis of $[Fe(TPPO)_4(OClO_3)_2](ClO_4)$ with no success. In all cases the complex originally obtained by Bannister and Cotton[1] was isolated. This complex exhibits the same splitting of ν_{M-O} (ligand) reported for the corresponding complexes of Mg^{II}, Mn^{II} and Ni^{II} perchlorates.[6,14] This may be attributed to the presence of both terminal and bridging TPPO groups.[17] Although the presence of weakly coordinated perchlorate has been claimed for the above compounds,[6] we believe that their formulation as $[M(TPPO)_4]_n(ClO_4)_{xn}$ (x = 2,3)[10,17] is more realistic, in view of the absence of any evidence for polyanion coordination[20,21] and the ν_{M-O} (ligand) splitting, which invariably occurs in pentacoordinated TPPO complexes of this type,[6,14] and is indicative of the presence of two sets of chemically non-equivalent TPPO groups. In fact, splittings of ν_{M-O} (ligand) have been reported in polynuclear ligand-bridged $[ML_2X_2]_n$ (M = Fe, Co, Ni; X = halide ion) complexes of phosphine and arsine oxides.[24] The two DMMP complexes exhibit a ν_{M-O} (ligand) band at 328–324 cm^{-1} (Table I). DMMP has a rich spectrum in the 300–250 cm^{-1} region (300s,b, 273m, 267sh, 262m, 248m–w), and if any ν_{M-O} (ligand) splitting occurs, the low frequency band may be masked by the above ligand absorptions. These complexes may also be formulated as $[M(DMMP)_4]_n(ClO_4)_{2n}$, on the basis of the above discussion and their electronic spectra,[7] which may be attributed to coordination number five for the central metal ions (Table II).[4–6,17]

The rest of the DMMP and TMP complexes studied are of the types $[ML_6](ClO_4)_n$ (M = Al^{III}, Cr^{III}, Mn^{II}, Fe^{III}; L = DMMP; M = Mg^{II}, Cr^{III}, Fe^{III}, L = TMP), $[ML_5](ClO_4)_2$ (M = Fe, L = DMMP; M = Mn, Fe, Co, Ni, Cu, Zn, L = TMP) and $[M(DMMP)_4(H_2O)_2](ClO_4)_2$ (M = Co, Zn) (Table I). The above formulations, which were previously established,[7,18] exclude any possibility of coordination of perchlorate. ν_{M-O} assignments (Table I, Fig. 2) are considered as reasonable, since the order of decrease of the ν_{M-O} frequency is $Al^{III} > Cr^{III} > Fe^{III} > Mn^{II}$ in hexacoordinated compounds and $Ni^{II} \sim Cu^{II} > Co^{II} > Fe^{II} > Mn^{II} \sim Zn^{II}$ in pentacoordinated complexes, as would be expected.[25] No metal–ligand bands could be identified in the hydrated Co^{II} and Zn^{II} complexes with DMMP.

In conclusion, recent conclusive evidence in favor of pentacoordinated configurations for non-tetrahedral $ML_4(ClO_4)_n$ complexes of phosphine and arsine

oxides[4–6, 14] led us to the re-examination of the properties of a number of organophosphoryl complexes with phosphonate and phosphate esters.[7, 18] These studies led to the conclusion that $M(DIMP)_4(ClO_4)_2$ complexes contain semi-coordinated perchlorate. These compounds were thus formulated as
$[M(DIMP)_4\ (OClO_3)](ClO_4)$. $Fe(TPPO)_4(ClO_4)_3$ and $M(DMMP)_4(ClO_4)_2$ (M = Ni, Cu) appear also to have coordination number higher than four, but do not exhibit any evidence in favor of coordination of perchlorate.[20, 21] The presence of a bi- or poly-nuclear complex cation, involving three terminal and one bridging organophosphoryl ligands per ML_4 moiety and coordination number five for the central metal ions,[17] is proposed for these compounds, which are formulated as $[ML_4]_n(ClO_4)_{xn}$.

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