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Two New Oxovanadium(V) Complexes with Hydrazone Ligands: Synthesis, Characterization, and Structure

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Two New Oxovanadium(V) Complexes with Hydrazone Ligands: Synthesis, Characterization, and Structure

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The reaction of [VO(acac)$_2$] with 3-methyl-*N*′-[1-(2-hydroxynaphthyl)ethylidene]benzohydrazide (H_2L^1) and 3-methyl-*N*′-[(2-hydroxy-1-naphthyl)methylidene]benzohydrazide (H_2L^2), respectively, in methanol affords two new oxovanadium(V) complexes, [VO(OMe)L^1]$_2$ (1) and [VO(OMe)(HOMe)L^2] (2). Both complexes have been characterized by elemental analysis, I.R., and single crystal X-ray diffraction methods. Complex (1) is a methoxide-bridged dinuclear oxovanadium(V) compound, while complex (2) is a mononuclear oxovanadium(V) compound. The dinegative hydrazone ligands coordinate to the metal atoms through phenolate, imine, and deprotonated amine donor atoms. The geometry around each vanadium atom is a distorted VNO_5 octahedron in both complexes.

Keywords crystal structure, hydrazone, synthesis, vanadium

INTRODUCTION

Oxovanadium(V) complexes with N- and O-containing ligands have been extensively investigated in recent years with respect to their remarkable efficiency as insulin mimetic compounds.[1–3] The interaction of simple vanadium species with ligands having pharmacological activity is of particular interest. Hydrazone compounds have been widely used as versatile ligands in coordination chemistry,[4–6] and they have shown interesting biological properties, such as antibacterial, antitumor, and antifungi activities.[7–9] In the present article, we describe the synthesis, spectroscopic characterization, and crystal structure determination of two new oxovanadium(V) complexes with similar tridentate hydrazone ligands, 3-methyl-*N*′-[1-(2-hydroxynaphthyl)ethylidene]benzohydrazide (H_2L^1) and 3-methyl-*N*′-[(2-hydroxy-1-naphthyl)methylidene] benzohydrazide (H_2L^2) (Scheme 1).

EXPERIMENTAL

Materials and Methods

2-Acetyl-1-naphthol, 2-hydroxy-1-naphthaldehyde, and 3-methylbenzhydrazide were purchased from Aldrich Chemical Co. All other reagent-grade chemicals and reagents were purchased commercially and used without further purification. Elemental analyses (C, H, N) were obtained with a Perkin-Elmer model 240C instrument. I.R. spectra were recorded in KBr discs on a Nicolet 170SX spectrophotometer.

Synthesis of the Hydrazone Compounds

H_2L^1: A mixture of 2-acetyl-1-naphthol (1.86 g, 10 mmol) and 3-methylbenzhydrazide (1.50 g, 10 mmol) in 100 mL of methanol was refluxed for 1 h. After reducing the solvent to 20 mL by distillation, and cooling to room temperature, the precipitated white solid was filtered off, washed with methanol, and dried in air. Recrystallization from methanol yielded pure product of H_2L^1. Yield 2.70 g (85%). Found: C, 75.37, H, 5.78; N, 8.72. Calc. for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. IR (KBr, cm^{-1}): 3437 (br, w), 3223 (m), 1640 (s), 1611 (m), 1602 (w), 1583 (m), 1560 (w), 1468 (m), 1413 (w), 1393 (w), 1364 (w), 1332 (m), 1291 (s), 1242 (w), 1213 (m), 1181 (m), 1137 (w), 963 (m), 845 (w), 827 (m), 787 (m), 747 (s), 672 (w), 663 (w).

H_2L^2: This compound was prepared by following the same procedure outlined for H_2L^1. The pure product was obtained as a white solid. Yield 2.65 g (87%). Found: C, 74.82, H, 5.36; N, 9.27. Calc. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. IR (KBr, cm^{-1}): 3448 (br, w), 3210 (m), 1645 (s), 1624 (m), 1602 (w), 1582 (m), 1560 (w), 1469 (m), 1415 (w), 1392 (w), 1364 (w), 1336 (m), 1297 (s), 1243 (w), 1215 (m), 1189 (m), 1143 (w), 1102 (w), 1031 (w), 960 (m), 859 (w), 822 (m), 799 (m), 745 (s), 689 (w), 651 (w), 546 (w).

Synthesis of the Vanadium(V) Complexes

[VO(OMe)L^1]$_2$ (1): [VO(acac)$_2$] (0.263 g, 1.0 mmol) dissolved in 20 mL methanol was added dropwise to a methanol solution (10 mL) of H_2L^1 (0.318 g, 1.0 mmol) with stirring, and then the mixture was heated at reflux with stirring for

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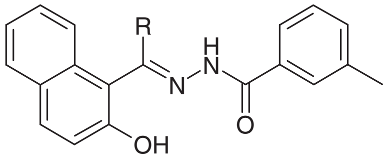

R = Me for H_2L^1 and R = H for H_2L^2

SCH. 1. The hydrazone ligands.

1 h and cooled to room temperature. When the solution was allowed to stand at room temperature for a few days to slow evaporation of the solvent, X-ray quality deep-red block-shaped single crystals were collected by filtration. The crystals were washed with methanol and dried in air. Yield 0.372 g (90%). Found: C, 60.67; H, 4.73; N, 6.83. Calc. for $C_{42}H_{38}N_4O_8V_2$: C, 60.88; H, 4.62; N, 6.76. IR (KBr, cm^{-1}): 1617 (w), 1592 (s), 1570 (s), 1538 (s), 1509 (m), 1449 (w), 1425 (s), 1371 (s), 1356 (m), 1337 (m), 1298 (w), 1287 (w), 1246 (s), 1214 (m), 1025 (s), 984 (s), 965 (m), 823 (m), 804 (w), 783 (w), 766 (w), 748 (m), 723 (s), 678 (w), 617 (s), 598 (s), 514 (w), 468 (w), 426 (w).

[VO(OMe)(HOMe)L^2] (2): This complex was prepared by following the same procedure outlined for (1). The X-ray quality deep-red block-shaped single crystals were obtained. Yield 0.323 g (75 %). Found: C, 58.16, H, 4.97; N, 6.60. Calc. for $C_{21}H_{21}N_2O_5V$: C, 58.34; H, 4.90; N, 6.48. IR (KBr, cm^{-1}): 3469 (br, w), 1616 (m), 1599 (s), 1546 (s), 1511 (s), 1478 (w), 1452 (m), 1421 (m), 1385 (m), 1361 (w), 1327 (s), 1284 (m), 1244 (w), 1223 (w), 1193 (w), 1143 (w), 1093 (w), 1046 (s), 1020 (m), 973 (s), 865 (m), 832 (m), 785 (w), 755 (s), 726 (m), 682 (w), 636 (s), 589 (s), 517 (w), 425 (w).

X-ray Structure Determination

The crystal and instrumental parameters used in the unit cell determination and data collection are summarized in Table 1. Diffraction measurements were made at room temperature on a Bruker SMART APEX II X-ray diffractometer using graphite-monochromated Mo Kα radiation using ω scan mode. Unit-cell dimensions were determined and refined in the range 1.80–27.00° for **(1)** and 1.71–27.00° for **(2)**. Both structures were solved by the direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F^2 with SHELXL-97.[10] The empirical absorption corrections were applied by the multi-scan method.[11] All non-hydrogen atoms were refined with anisotropic displacement parameters. The methanol H atom in **(2)** was located in a difference Fourier map, and refined isotropically, with O–H distance restrained to 0.85(1) Å, and with U_{iso} restrained to 0.08 Å^2. The remaining hydrogen atoms were included in their idealized positions and refined isotropically. Selected bond distances (Å) and angles (°) for the complexes are listed in Table 2.

TABLE 1

Crystallographic data for the complexes

	(1)	**(2)**
Formula	$C_{42}H_{38}N_4O_8V_2$	$C_{21}H_{21}N_2O_5V$
Mr	828.6	432.3
Crystal size (mm)	0.23 × 0.20 × 0.20	0.30 × 0.27 × 0.27
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1/n$
a (Å)	7.8730(16)	12.796(2)
b (Å)	10.962(2)	8.6638(14)
c (Å)	11.360(2)	18.840(3)
α (°)	87.03(3)	90
β (°)	86.20(3)	108.208(2)
γ (°)	73.35(3)	90
V (Å^3)	936.7(3)	1984.1(6)
Z	1	4
D_c (g/cm^3)	1.469	1.447
μ (mm^{-1})	0.560	0.536
F (000)	428	896
Temperature (K)	298(2)	298(2)
T_{min}	0.8820	0.8559
T_{max}	0.8962	0.8689
Reflections measured	7790	15450
Independent reflections (R_{int})	3888	4241
Observed reflections	3338	3376
Goodness of fit on F^2	1.015	1.034
Final R indices [$I \geq 2\sigma(I)$]^a	$R_1 = 0.0388$ $wR_2 = 0.1004$	$R_1 = 0.0461$ $wR_2 = 0.1112$
R indices (all data)^a	$R_1 = 0.0456$ $wR_2 = 0.1046$	$R_1 = 0.0608$ $wR_2 = 0.1196$

$^a R_1 = \sum||Fo| - |Fc||/\sum|Fo|$, $wR_2 = [\sum w(Fo^2 - Fc^2)^2/\sum w(Fo^2)^2]^{1/2}$

RESULTS AND DISCUSSION

The hydrazone compounds were prepared by the condensation of similar carbonyl-containing compounds with 3-methylbenzhydrazide in methanol. Each of them has two dissociable protons at the phenolic-OH and the amide functionality. The reaction of bis(acetylacetonato)oxovanadium(IV) with stoichiometric amounts of the hydrazone ligands in methanol in air afforded the two vanadium(V) complexes as deep-red crystalline solids. It should be pointed out that the vanadium in the starting materials is in V(IV) oxidation state, but it appears to be V(V) in both complexes, indicating that it was oxidized by air during the reaction procedures. Elemental analyses of the complexes are satisfactory with the empirical formulae.

Spectra Characterization of the Complexes

The I.R. spectra of the ligands exhibit two bands in the regions 3210–3230 and 1640–1645 cm^{-1} due to the ν(N-H) and υ(C=O) stretches.[12] The absence of these bands in the spectra of the complexes is consistent with the enolisation of the amide functionality and subsequent proton replacement by the vanadium atom. A broad and weak band observed at 3469 cm^{-1} in the infrared spectrum of **(2)** due to the O-H stretch of the

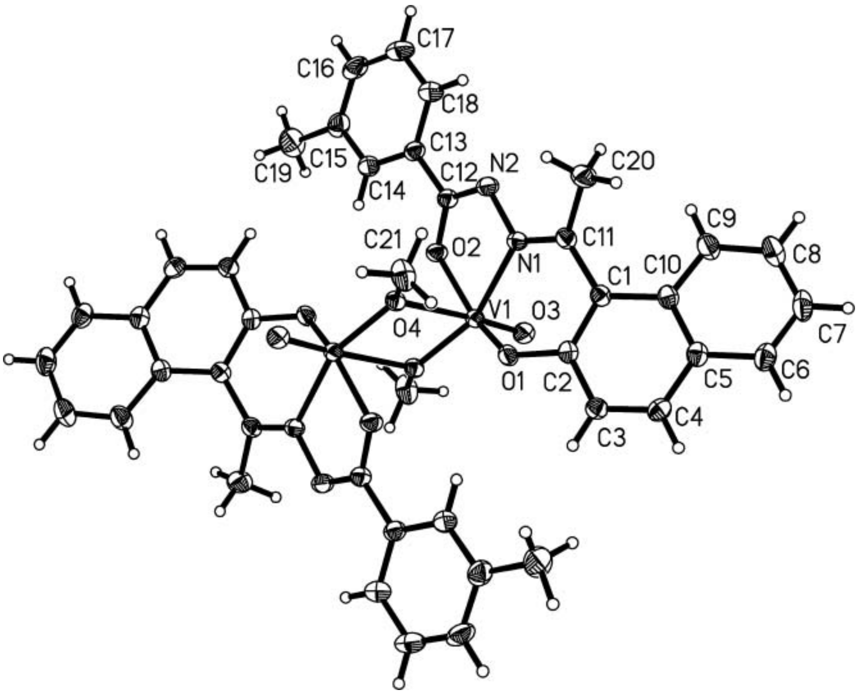

FIG. 1. Molecular structure of (**1**) with 30% thermal ellipsoids. Unlabelled atoms are related to the symmetry operation $-x$, $1-y$, $2-z$.

coordinated MeOH is absent in the spectrum of (**1**). A new band appearing in the 1244–1287 cm^{-1} range is assigned to the ν(C-O)(enolic) mode. The strong bands at 1592 and 1599 cm^{-1} in complexes (**1**) and (**2**), respectively, with shoulders are assigned to the conjugate C=N-N=C moieties.[13]The bands observed at 984 and 973 cm^{-1} for (**1**) and (**2**), respectively, are assigned to the V=O stretch.[12,14]

Structure Description of (1)

The molecular structure of (**1**) is shown in Figure 1. The complex is a methoxide oxygen-bridged centrosymmetric dinuclear vanadium(V) compound. The V···V distance is 3.363(2) Å. The dianionic tridentate hydrazone ligand binds the metal atom through the phenolate-O, imine-N, and deprotonated amide-O atoms, forming a six- and a five-membered chelate rings, which are inclined to each other by 15.5(3)°. Each V atom is in a distorted NO_5 octahedral coordination, with the three donor atoms of the hydrazone ligand and one methoxide O atom defining the equatorial plane, and with one oxo O and one symmetry-related methoxide O atom occupying the axial positions. The mean deviation of the four equatorial donor atoms from the least-squares plane is 0.010(3) Å. The displacement of the V atom towards

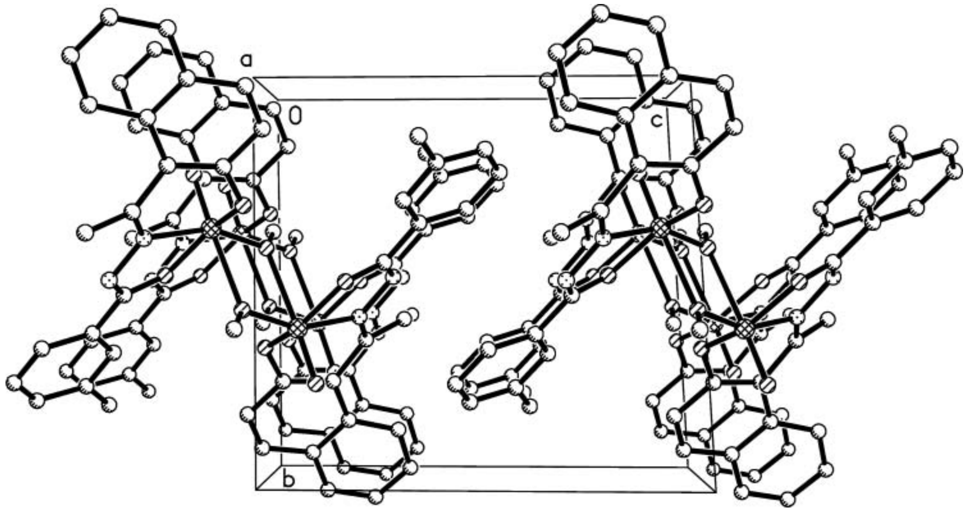

FIG. 2. Molecular packing of (**1**), viewed along the *a* axis.

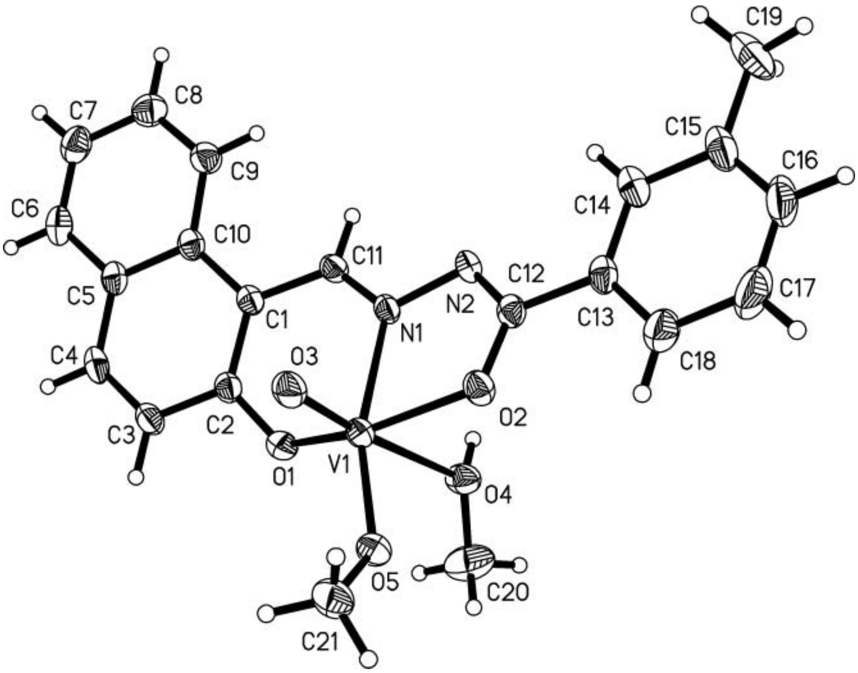

FIG. 3. Molecular structure of (**2**) with 30% thermal ellipsoids.

TABLE 2
Selected bond lengths (Å) and bond angles (°) for the complexes

(**1**)		(**2**)	
V1-O1	1.8361(15)	V1-O1	1.8649(17)
V1-O2	1.9210(16)	V1-O2	1.9579(16)
V1-O3	1.5844(16)	V1-O3	1.5795(17)
V1-O4	2.3556(15)	V1-O4	2.3422(18)
V1-O4A	1.8261(15)	V1-O5	1.7646(18)
V1-N1	2.0941(17)	V1-N1	2.1041(19)
O1-V1-O2	150.00(7)	O1-V1-O2	151.82(7)
O3-V1-O1	101.05(8)	O3-V1-O1	99.16(9)
O3-V1-O2	100.55(8)	O3-V1-O2	98.61(8)
O3-V1-O4A	103.22(8)	O3-V1-O5	102.09(9)
O4A-V1-O1	103.46(6)	O5-V1-O1	102.85(8)
O4A-V1-O2	91.53(7)	O5-V1-O2	94.57(8)
O3-V1-N1	97.14(8)	O3-V1-N1	94.63(8)
O4A-V1-N1	157.23(7)	O5-V1-N1	161.16(8)
O1-V1-N1	82.24(7)	O1-V1-N1	82.74(7)
O2-V1-N1	74.63(7)	O2-V1-N1	74.17(7)
O3-V1-O4	176.76(6)	O3-V1-O4	174.72(8)
O4-V1-O4A	73.64(6)	O5-V1-O4	82.25(7)
O1-V1-O4	79.12(6)	O1-V1-O4	82.65(7)
O2-V1-O4	80.48(6)	O2-V1-O4	77.90(7)
N1-V1-O4	86.10(6)	N1-V1-O4	80.64(7)

Symmetry code for A: – *x*, 1 – *y*, 2 – *z*.

the oxo group from the plane is 0.355(2) Å. The distances of V=O and other coordination bonds in the complex are within the range of similar vanadium(V) complexes.[15,16]

In the crystal structure of **(1)**, molecules are stacked along the *a* axis, with no obvious short contacts (Figure 2).

Structure Description of (2)

The molecular structure of **(2)** is shown in Figure 3. The methoxide ligand lies *trans* to the imine-N atom. The methanol ligand is coordinated *trans* to the oxo group. The dianionic tridentate hydrazone ligand binds the metal atom through the phenolate-O, imine-N, and deprotonated amide-O atoms, forming a six- and a five-membered chelate rings, which are inclined to each other by 11.4(3)°. The V atom is in a distorted NO_5 octahedral coordination, with the three donor atoms of the hydrazone ligand, and one methoxide O atom defining the equatorial plane, and with one oxo O and one methanol O atom occupying the axial positions. The mean deviation of the four equatorial donor atoms from the least-squares plane is 0.017(3) Å. The displacement of the V atom towards the oxo group from the plane is 0.296(2) Å. The distances of V=O and other coordination bonds in the complex are within the range of similar vanadium(V) complexes.[17–19]

In the crystal structure of **(2)**, adjacent two molecules are linked through intermolecular O–H· · ·N hydrogen bonds (O4–H4A = 0.847(10) Å, H4A· · ·N2 = 1.994(12) Å, O4· · ·N2 = 2.833(3) Å; O4-H4A-N2 = 170(3)°), forming a dimer (Figure 4).

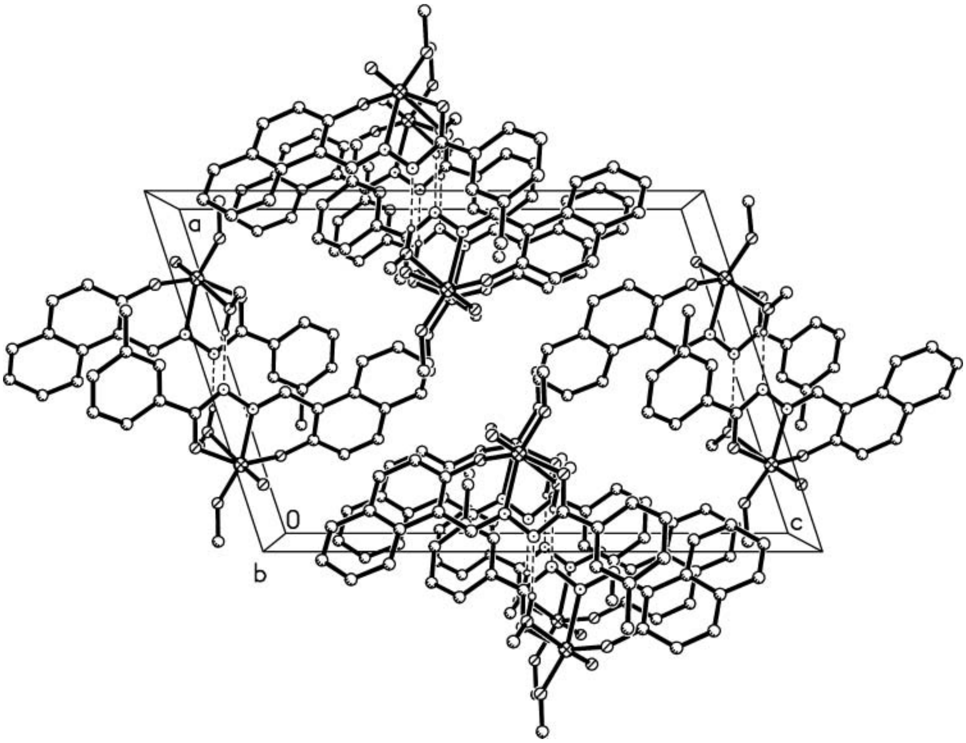

FIG. 4. Hydrogen bonded dimers of (**2**), viewed along the *b* axis.

In both complexes, the N2-C12 and C12-O2 bond lengths in the five-membered chelate rings are consistent with the enolate form of the amide functionality. The corresponding bond values are comparable to each other. The difference in the molecular structures of the two complexes in solid state may arise due to the crystal packing forces or bulk solid state effects mediated by the differing substitute groups.

CONCLUSIONS

The results presented here clearly show that the hydrazone compounds 3-methyl-*N*′-[1-(2-hydroxynaphthyl) ethylidene]benzohydrazide and 3-methyl-*N*′-[(2-hydroxy-1-naphthyl)methylidene]benzohydrazide can be used as versatile tridentate ligands for the preparation of vanadium(V) complexes. The slight difference between the hydrazone compounds can result in severely different vanadium(V) structures. Further work needs to be carried out to understand the rules of the self-assembly of such complexes.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-790971 (1) and no. CCDC-790972 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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