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The Crystal and Molecular Structure of μ-(*N*-Salicylidene-L-valinato-*O*)-*N*-salicylidene-L-valinatodiaquadicopper(II)

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The structure of the Schiff base-type complex μ-(*N*-salicylidene-L-valinato-*O*)-*N*-salicylidene-L-valinatodiaquadicopper(II) [$a = 7.38(3)$ Å, $b = 12.90(5)$ Å, $c = 27.53(6)$ Å, $Z = 8$, space group $P2_12_12_1$] has been solved by three-dimensional Fourier methods and refined by block-diagonal least-squares technique, hydrogen atoms excluded, to the R value 0.089. The asymmetric part of the unit cell contains two formula units joined to a dimer. The coordination sphere around one copper(II) atom (Cu1) is square pyramidal (4 + 1) and around the other (Cu2) square planar. The *N*-salicylidene-L-valinato group occupies three positions of the basal plane around the Cu1 atom and the oxygen atom of a coordinated water molecule the fourth [Cu1 – O1 = 1.92(1), Cu1 – N1 = 1.91(1), Cu1 – O3 = 1.89(1) and Cu1 – O4 = 1.94(1) Å]. An oxygen atom of the adjacent carboxylate group occupies the axial position [Cu1 – O5 = 2.61(1) Å]. The basal plane around the Cu2 atom consists of three atoms from the second *N*-salicylidene-L-valinato group and the oxygen atom of the second coordinated water molecule [Cu2 – O5 = 1.94(1), Cu2 – N2 = 1.90(1), Cu2 – O7 = 1.87(1) and Cu2 – O8 = 1.96(1) Å]. The oxygen atom (O5) of the carboxylate group acts as a bridging atom between the Cu1 and Cu2 atoms joining together the approximately planar complex molecules in the asymmetric unit at 88.5°.

Transition metal complexes of salicylaldehyde-amino acid Schiff bases are analogous to those of pyridoxal-amino acid Schiff bases, which are of considerable biological importance in nonenzymatic catalyzed transamination reactions.[1–3] Structures of transition metal complexes of salicylaldehyde-amino acid Schiff bases are also possible model compounds in some toxicological investigations. Earlier a few crystal structures of metal complexes with Schiff bases have been solved.[4–8] Those of copper(II) complexes formed with salicylaldehyde and L-tyrosine or L-phenylalanine have been investigated in this laboratory.[7,8] Some analogous copper(II) complexes formed with L-amino acids and salicylaldehyde have also been crystallized and structure analyses are in progress. Carlisle *et al.* have prepared the *N*-salicylidene-L-valinatocopper(II) complex in crystalline state and on the basis of magnetic properties have described the structure as tetranuclear.[9,10] In this study we present the structure of μ-(*N*-salicylidene-L-valinato-*O*)-*N*-salicylidene-L-valinatodiaquadicopper(II).

EXPERIMENTAL

Preparation. 0.01 mol of salicylaldehyde in 10 cm^3 ethanol was added to 50 cm^3 warm (60 °C) water containing 0.01 mol of L-valine (E. Merck AG). The mixture was stirred at this temperature until clear and 0.01 mol of copper(II) acetate monohydrate was added. Stirring was continued until all copper(II) acetate was dissolved. The dark green solution was left to evaporate at room temperature (25 °C). After about one week the crude product was precipitated as fine needles. The filtered compound was recrystallized from water at 50 °C and dark green, prismatic crystals were obtained. Copper was analyzed electrolytically. Calc. for $C_{12}H_{15}CuNO_4$: Cu 21.12 %, found 21.08 %.

Unit cell and intensity measurements. Equi-inclination Weissenberg photographs showed systematic absences of $h00$, $0k0$ and $00l$ reflections with h, k and l odd, indicating the orthorhombic space group $P2_12_12_1$ (No. 19).[11] The cell dimensions were calculated by least-squares analysis of the angular settings of 13 reflections, using a SYNTEX

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$P2_1$ diffractometer and Mo$K\alpha$ radiation. Crystal data are:

a = 7.38(3) Å
b = 12.90(5) Å
c = 27.53(6) Å
V = 2621 Å^3

F.W. = 300.79
Z = 8
D_{calc} = 1.530 g cm^{-3}
D_{obs} = 1.53 g cm^{-3} (by flotation method)
Space group $P2_12_12_1$

The intensities of 3808 reflections from a crystal of dimensions 0.2 × 0.3 × 0.8 mm were measured using the ω-scan technique with variable scan speed (2.0 to 15.0° min^{-1}) and graphite monochromatized Mo$K\alpha$ radiation (λ=0.71069 Å). Two selected reflections were monitored periodically (after every 60 reflections) to check for possible variations. The data were corrected for Lorentz and polarization effects but not for absorption [μ(Mo$K\alpha$)=17.4 cm^{-1}].

Structure determination. The MULTAN-74 programs[12] and the XRAY-76 program system[13] were used in solving the structure. The coordination

Table 1. Fractional atomic coordinates (× 10^4) and thermal parameters[a] (× 10^3) with their standard deviations in parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu1	4026(2)	6927(2)	979(1)	15(1)	49(1)	25(1)	3(1)	−1(1)	2(1)
Cu2	5583(3)	3911(2)	854(1)	20(1)	38(1)	57(1)	1(1)	−1(1)	−7(1)
O1	2113(15)	7254(11)	534(4)	19(5)	71(9)	25(5)	6(6)	4(2)	8(5)
O2	−781(16)	7577(12)	480(4)	16(6)	94(11)	36(6)	−1(7)	−7(5)	13(6)
O3	5905(16)	6595(10)	1420(4)	24(6)	57(8)	26(5)	6(6)	2(5)	7(5)
O4	5662(16)	6969(12)	428(4)	17(6)	78(9)	38(6)	5(8)	2(5)	12(6)
O5	3706(13)	4912(8)	1007(4)	16(5)	27(5)	54(6)	3(4)	4(5)	9(5)
O6	767(18)	5100(12)	1122(5)	14(6)	61(9)	97(11)	2(7)	6(7)	−15(8)
O7	7330(17)	2960(11)	643(6)	24(7)	42(8)	107(11)	−1(7)	−6(7)	−31(8)
O8	7366(16)	5035(11)	894(6)	22(6)	50(8)	89(10)	−2(6)	7(7)	−17(8)
N1	2239(19)	7134(11)	1469(4)	28(7)	36(8)	23(6)	5(6)	−3(5)	−11(5)
N2	3664(18)	2928(11)	876(5)	19(6)	41(8)	51(8)	5(6)	−1(6)	−5(7)
C1	579(23)	7463(14)	726(6)	21(8)	38(9)	54(10)	−9(8)	−5(7)	−1(8)
C2	484(22)	7541(14)	1282(6)	16(8)	49(10)	34(8)	1(8)	1(6)	4(7)
C3	176(30)	8624(16)	1458(8)	41(12)	44(12)	69(13)	14(10)	4(9)	−6(10)
C4	1433(32)	9410(16)	1213(7)	59(14)	38(11)	61(12)	−14(11)	−14(10)	14(9)
C5	−1831(33)	8987(20)	1415(10)	51(14)	50(14)	107(18)	14(14)	−8(12)	−19(13)
C6	2367(24)	6868(16)	1923(6)	32(9)	46(11)	35(8)	5(10)	1(7)	1(8)
C7	3965(24)	6420(14)	2133(5)	30(9)	46(10)	28(7)	6(8)	−15(7)	2(7)
C8	3807(30)	6074(22)	2620(6)	52(12)	111(19)	30(8)	10(15)	−6(9)	29(11)
C9	5317(40)	5658(23)	2866(7)	80(18)	120(21)	31(11)	28(17)	−11(11)	1(12)
C10	6932(32)	5508(20)	2623(7)	49(12)	85(17)	43(11)	−9(13)	−26(10)	16(11)
C11	7102(28)	5844(18)	2125(7)	35(10)	65(15)	55(11)	4(10)	−5(9)	14(10)
C12	5636(26)	6284(13)	1882(5)	37(9)	37(9)	26(7)	−4(9)	−13(7)	6(6)
C13	2133(24)	4534(14)	1061(6)	25(8)	40(10)	51(10)	−8(8)	9(7)	−18(8)
C14	1971(25)	3331(13)	1091(7)	35(9)	14(8)	76(12)	−14(7)	11(8)	−1(7)
C15	1793(33)	2889(20)	1616(8)	53(13)	79(17)	57(12)	−2(13)	18(10)	26(12)
C16	3185(44)	3427(20)	1955(8)	130(23)	64(15)	44(11)	−40(16)	−25(13)	10(10)
C17	9853(39)	3112(28)	1817(11)	68(17)	116(25)	93(19)	−8(20)	24(14)	−1(19)
C18	3702(26)	1989(15)	712(7)	39(10)	30(9)	61(11)	−1(9)	−9(8)	5(8)
C19	5272(29)	1524(16)	517(7)	50(12)	47(11)	45(10)	−2(10)	−10(9)	−1(8)
C20	5135(34)	476(17)	336(8)	62(15)	41(12)	65(13)	1(11)	6(11)	8(10)
C21	6578(41)	−93(20)	160(8)	91(20)	65(16)	49(11)	23(15)	−1(12)	−13(11)
C22	8348(38)	386(19)	182(7)	89(18)	60(15)	35(9)	34(14)	4(10)	1(9)
C23	8462(31)	1428(17)	343(8)	47(13)	52(12)	62(12)	17(11)	−10(10)	−3(10)
C24	7027(26)	1998(19)	508(7)	31(10)	69(15)	57(11)	−15(11)	−1(8)	−1(11)

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+\ldots+2hka^*b^*U_{12}+\ldots)]$.

Table 2. Interatomic distances (Å) and angles (°) with standard deviations in parentheses. The labelling of atoms is in accordance with Fig. 1.

Complex molecule	*A*	Complex molecule	*B*
Cu1 – O1	1.92(1)	Cu2 – O5	1.94(1)
Cu1 – N1	1.91(1)	Cu2 – N2	1.90(1)
Cu1 – O3	1.89(1)	Cu2 – O7	1.87(1)
Cu1 – O4	1.94(1)	Cu2 – O8	1.96(1)
Cu1 – O5	2.61(1)		
O1 – C1	1.28(2)	O5 – C13	1.27(2)
O2 – C1	1.22(2)	O6 – C13	1.26(2)
O3 – C12	1.35(2)	O7 – C24	1.32(2)
N1 – C2	1.49(2)	N2 – C14	1.48(2)
N1 – C6	1.30(2)	N2 – C18	1.29(2)
C1 – C2	1.54(2)	C13 – C14	1.56(3)
C2 – C3	1.50(3)	C14 – C15	1.56(3)
C3 – C4	1.53(3)	C15 – C16	1.55(4)
C3 – C5	1.56(3)	C15 – C17	1.56(4)
C6 – C7	1.43(3)	C18 – C19	1.41(3)
C7 – C8	1.42(2)	C19 – C20	1.44(3)
C7 – C12	1.43(3)	C19 – C24	1.43(3)
C8 – C9	1.41(4)	C20 – C21	1.38(4)
C9 – C10	1.38(4)	C21 – C22	1.45(4)
C10 – C11	1.44(3)	C22 – C23	1.42(3)
C11 – C12	1.39(3)	C23 – C24	1.37(3)
O1 – Cu1 – N1	85.0(5)	O5 – Cu2 – N2	84.6(5)
O1 – Cu1 – O3	179.6(6)	O5 – Cu2 – O7	174.6(6)
O1 – Cu1 – O4	87.3(5)	O5 – Cu2 – O8	88.5(5)
N1 – Cu1 – O3	94.8(5)	N2 – Cu2 – O7	94.9(6)
N1 – Cu1 – O4	168.7(6)	N2 – Cu2 – O8	172.2(6)
O3 – Cu1 – O4	93.0(5)	O7 – Cu2 – O8	92.3(6)
O1 – Cu1 – O5	99.9(5)		
N1 – Cu1 – O5	93.2(5)		
O3 – Cu1 – O5	79.8(5)		
O4 – Cu1 – O5	96.1(5)		
O1 – C1 – O2	121.6(16)	O5 – C13 – O6	121.8(17)
O1 – C1 – C2	117.8(14)	O5 – C13 – C14	117.4(15)
O2 – C1 – C2	120.6(15)	O6 – C13 – C14	120.7(16)
C1 – C2 – C3	112.9(15)	C13 – C14 – C15	114.8(16)
C1 – C2 – N1	106.4(13)	C13 – C14 – N2	108.3(16)
C2 – C3 – C4	112.6(17)	C14 – C15 – C16	109.8(19)
C2 – C3 – C5	113.6(18)	C14 – C15 – C17	109.8(20)
C4 – C3 – C5	110.1(18)	C16 – C15 – C17	108.2(21)
C2 – N1 – C6	119.3(14)	C14 – N2 – C18	119.2(15)
N1 – C6 – C7	123.6(16)	N2 – C18 – C19	123.3(18)
C6 – C7 – C8	116.1(16)	C18 – C19 – C20	118.2(19)
C6 – C7 – C12	124.4(14)	C18 – C19 – C24	124.5(19)
C8 – C7 – C12	119.4(16)	C20 – C19 – C24	117.2(20)
C7 – C8 – C9	120.7(19)	C19 – C20 – C21	124.4(23)
C8 – C9 – C10	120.0(19)	C20 – C21 – C22	117.0(22)
C9 – C10 – C11	119.6(21)	C21 – C22 – C23	118.2(23)
C10 – C11 – C12	120.8(19)	C22 – C23 – C24	124.6(22)
C7 – C12 – C11	119.2(15)	C19 – C24 – C23	118.4(21)
O3 – C12 – C7	123.3(15)	O7 – C24 – C19	123.5(19)
O3 – C12 – C11	117.4(16)	O7 – C24 – C23	118.1(19)

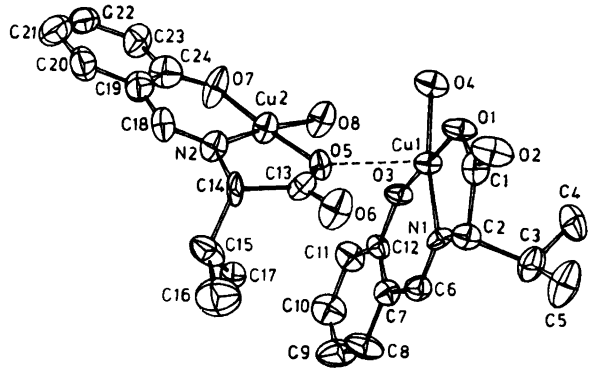

Fig. 1. The structure and numbering scheme of the compound. Thermal ellipsoids are scaled to enclose 50 % probability.

spheres around copper(II) atoms were located from a first Fourier summation phased on the copper atoms. The remaining atoms of the structure were located by successive Fourier syntheses. The refinement of the structure was carried out by block-diagonal least-squares method with isotropic thermal parameters to the R value 0.142 and with anisotropic parameters to $R=0.089$ ($R=\sum\|F_o|-|F_c\|/\sum|F_o|$). The 2251 reflections having $I>2\delta(I)$ were included in the refinement. Attempts were made to locate the hydrogen atoms from a difference Fourier map, but only some could be located unambiguously and therefore the hydrogen atoms were excluded from the calculations. The weighting scheme used was $w=1/(50.0+|F_o|+0.005|F_o|^2)$ and the function minimized of the form $\sum w(|F_o|-|F_c|)^2$. The scattering factors for the nonhydrogen atoms were from Cromer and Mann.[14] Anomalous dispersion corrections were applied for the copper atoms, using the values of $\Delta f'$ and $\Delta f''$ given by Cromer and Liberman.[15] Calculations were carried out on a UNIVAC 1108 computer.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters with their standard deviations are given in Table 1 and the numbering scheme of the asymmetric unit is shown in Fig. 1. A list of observed and calculated structure factors is obtainable on request from the authors.

The coordination distances and angles around the copper(II) atoms of the asymmetric unit are given in Table 2. These values are comparable with those found earlier in related compounds.[4-8]

The coordination geometry around one copper(II) atom (Cu1) is distorted square-pyramidal (4+1).

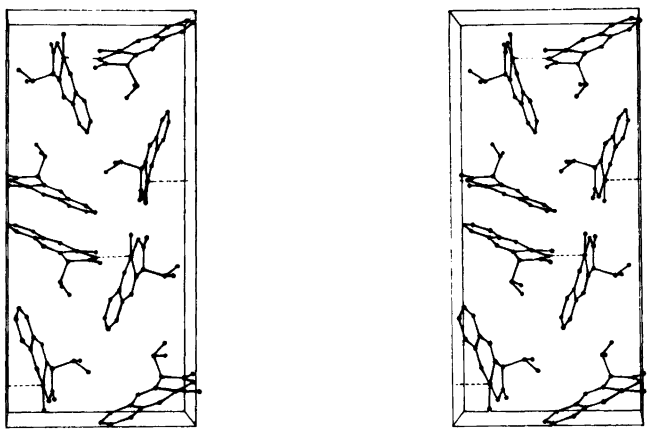

Fig. 2. Stereoscopic view of the unit cell along the a axis. The b axis is horizontal, the c axis is vertical.

Table 3. Deviations (Å) from least-squares planes. Atoms indicated with an asterisk were omitted from the calculation of the planes.

Plane 1	O1	−.075	Cu1*	−.065
	N1	.072	O5*	2.633
	O3	.070		
	O4	−.067		
Plane 2	O1	−.003	Cu1*	−.217
	O2	−.003	N1*	−.294
	C1	.007	O3*	−.440
	C2	−.002	O4*	.165
Plane 3	C7	.011	Cu1*	−.349
	C8	−.021	O1*	−.747
	C9	.022	N1*	−.079
	C10	−.012	O3*	.034
	C11	.001	O4*	−.410
	C12	−.001	C6*	.017
Plane 4	O5	−.076	Cu2*	.017
	N2	.075	Cu1*	−.618
	O7	−.070	N1*	.398
	O8	.071	O3*	.881
Plane 5	O5	.009	Cu2*	−.230
	O6	.009	Cu1*	.022
	C13	−.025	N2*	−.403
	C14	.007	O7*	−.635
			O8*	.102
Plane 6	C19	.014	Cu2*	−.148
	C20	.004	O5*	−.424
	C21	−.024	N2*	.119
	C22	.028	O7*	−.054
	C23	−.011	O8*	−.334
	C24	−.010	C18*	.122

Angles (°) between	plane 1 and 2	9.8
	1 and 3	12.8
	1 and 4	87.1
	2 and 3	22.2
	2 and 5	89.3
	3 and 6	89.1
	4 and 5	22.2
	4 and 6	8.8
	5 and 6	21.3

The tridentate *N*-salicylidene-L-valinato group occupies three of the square-planar coordination sites and the oxygen atom O4 of a water molecule completes the plane. The carboxyl oxygen atom O5 of the adjacent complex occupies the apical site at a distance of 2.61 Å.

Around the other copper(II) atom (Cu2), the coordination geometry is square-planar. Three of the coordination sites are occupied by the *N*-salicylidene-L-valinato group and the fourth site is occupied by the oxygen atom O8 of a water molecule. The methyl carbon atom C16 of the isopropyl group at the distance 3.56 Å and the carbon atoms C22 and C23 of the benzene ring of the adjacent complex at distances 3.42 and 3.67 Å, respectively, hinder the formation of an octahedral coordination around this copper atom. Likewise, the methyl carbon atom C4 at a distance of 3.79 Å prevents formation of the octahedral coordination around the Cu1 atom (Figs. 1 and 2).

The Cu1 – Cu2 bond distance is 4.07 Å, which is clearly less than, for instance, the closest Cu – Cu distance, 4.36 Å, in *catena*-μ-(*N*-salicylidene-L-tyrosinato-*O,O'*)copper(II).[7]

Each complex molecule consists of three approximately planar groups: the atoms of the coordination plane, the carboxylate group, and the benzene ring of the salicylidene residue. The displacement of selected atoms from least-squares planes and the angles between the planes are presented in Table 3. The Cu1 atom is situated almost in the coordination plane, the deviation being 0.07 Å. The deviation of the Cu2 atom is far less (0.02 Å) than the deviations of the plane atoms themselves. Thus the deviations of both central copper(II) atoms from the square coordination plane around them are far less than the 0.23 Å in *N*-salicylideneglycinatoaquacopper(II) hemihydrate,[4] 0.14 Å in *N*-salicylideneglycinatoaquacopper(II) tetrahydrate,[5] 0.18 – 0.20 Å in *N*-salicylidene-L-phenylalaninatoaquacopper(II) dimer,[8] and 0.20 Å in *N*-salicylidene-α-aminoisobutyratocopper(II),[6] and of the same magnitude (0.06 Å) as in *catena*-μ-(*N*-salicylidene-L-tyrosinato-*O,O'*)copper(II).[7]

The mean values for the bond lengths in the benzene rings (Table 2) are 1.41 and 1.42 Å, respectively. The planarity of both aromatic rings is satisfactory. The planarity of the carboxylate group (O1, O2, C1 and C2) in one complex molecule (A) is better than the planarity of the corresponding group (O5, O6, C13 and C14) in the other complex (B), where the deviations from the least-squares plane are three times greater. Moreover, in the latter carboxylate group (molecule B) the oxygen-carbon distances are practically the same [O5 – C13 = 1.27(2) Å and O6 – C13 = 1.26(2) Å], whereas in the former complex (A) the distance from the carboxylate carbon atom C1 to the uncoordinated

oxygen atom O2 is smaller [1.22(2) Å] than that to the coordinated oxygen atom O1 [1.28(2) Å]. The equality in the former case is probably due to the fact that the O5 atom is coordinated not only to the Cu2 atom but also connected to the copper atom Cu1. However, both the rather long Cu1 – O5 distance (2.61 Å) and the fact that the Cu1 atom is situated in its coordination plane indicate a rather weak Cu1 – O5 interaction.

The Cu1 – O5 bond is almost perpendicular to the least-squares coordination plane. The coordination, carboxylate and benzene ring least-squares planes of the two complex molecules are likewise nearly perpendicular to each, as can be seen in Table 3, and thus the two monomers as a whole, isopropyl groups excluded, are almost perpendicular to each other (88.5°), connected *via* the oxygen atom O5.

There are no significant differences in corresponding bond lengths and angles in the two complexes of the asymmetric unit, if standard deviations are taken into account.

In copper(II) complexes formed with salicylaldehyde and glycine,[4,5] L-tyrosine[7] and L-phenylalanine,[8] the bond between the nitrogen atom and the carbon atom of the amino acid part has been found to be shorter than the normal single bond (1.47 – 1.49 Å), while the bond between the nitrogen atom and the carbon atom of the aldehyde part has the usual N=C bond distance (1.29 – 1.30 Å). In *N*-salicylidene-α-aminoisobutyratoaquacopper-(II),[6] on the other hand, the N – C single bonds have normal values and the N=C double bonds are shorter than the usual double bonds. In the title compound both the N – C single bonds and the N=C double bonds (1.49 – 1.50 and 1.29 – 1.30 Å, respectively; Table 2) have normal values, within error limits.

Table 4 presents selected intermolecular distances of the asymmetric unit and Table 5 intermolecular distances between adjacent asymmetric units. As can be seen in Tables 4 and 5, the water molecules O4 and O8 are engaged in hydrogen bond formation.

Table 4. Selected intermolecular distances (Å) in the asymmetric unit less than 3.5 Å with standard deviations in parentheses.

Cu1 – O6	3.39(1)	O3 – O8	2.70(2)
Cu1 – O8	3.48(1)	O4 – O5	3.42(2)
O1 – O5	3.49(2)	O4 – O8	3.07(2)
O1 – O6	3.36(2)	N1 – O5	3.32(2)

Table 5. Intermolecular distances (Å) between adjacent asymmetric units less than 3.5 Å with standard deviations in parentheses.

$O4-O2_{I}$	2.74(2)	$C21-O1_{III}$	3.40(3)
$O4-O2_{II}$	2.78(2)	$C22-Cu2_{III}$	3.42(2)
$O4-O1_{II}$	3.03(2)	$C22-O5_{III}$	3.31(2)
$O1-O2_{II}$	3.20(2)	$C23-N2_{III}$	3.46(3)

I = $x+1,y,z$
II = $x+1/2,-y+3/2,-z$
III = $x+1/2,-y+1/2,-z$

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