A novel tetranuclear copper(II) cluster containing twisted hydrazide bridges. X-ray crystal structure and magnetic properties of tetrakis[*N,N'*-imidopicolinyloxamylhydrazine)copper(II)] tetranitrate octahydrate

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Abstract

A novel tetranuclear copper(II) cluster of formula $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$ is reported containing the anion of *N,N'*-imidopicolinyloxamylhydrazine as a dinucleating bis(didentate) ligand. The tetrahedral cluster has crystallographic S_4 symmetry and is flattened along one of the C_2 axes. The copper(II) ions are located on its vertices. The title compound crystallizes in the tetragonal space group $I4_1/a$, $a=19.334(4)$, $c=15.257(13)$ Å, $\alpha=\beta=\gamma=90°$, $V=5703$ Å^3, $Z=4$ (tetranuclear units). Each copper(II) is in a distorted square pyramidal environment consisting of three nitrogen atoms and one oxygen atom from the ligand, and an apical oxygen from a nitrate at 2.01(2) Å. Some relevant interatomic distances are Cu–N = 1.95(1), Cu–O = 1.96(1), Cu–Cu' = Cu–Cu'' = 4.456(4), Cu–Cu''' = 3.435(4) Å. The X-band powder EPR spectra at 298 and 77 K show an isotropic signal at $g=2.09$. The magnetic susceptibility measurements (6.5–280 K) indicate that there is no significant magnetic interaction between the metal ions; this behaviour can be understood on the basis of orthogonal magnetic orbitals within the cluster.

Introduction

Tetranuclear copper(II) clusters are well known in coordination chemistry and have been subject of numerous studies of magnetic superexchange interactions. Several structure types have been reported in the last decade, e.g. halide-bridged clusters, in which the metal ions are in a tetrahedral arrangement, bridged over the edges by halide ions and by an oxygen atom in the centre of the tetrahedron [1, 2]. A second type is the cubane-type cluster. Here the metal ions are linked by oxygen atoms in a Cu_4O_4 unit [3–5]. Recently, a different type of tetranuclear copper(II) cluster has been reported [6, 7], in which the copper(II) ions are linked by the 3-(pyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazolato anion. In fact that compound represented the first example of a tetranuclear cluster compound with only diatomic bridges.

The present new ligand, *N,N'*-imidopicolinyloxamylhydrazine (abbreviated as Himp) is an intermediate in the synthesis of 1,2,4-triazole ligands. The coordination chemistry of such open-ring systems has been found to be interesting, and it was decided to investigate its behaviour towards Cu(II) salts. The Himp ligand is much more flexible compared to the triazole ligands and, moreover, it has the possibility to twist around the N–N bond allowing flexible coordination modes. The ligand has several potential donor atoms, which makes it readily available for a variety of coordination modes, including bridging between metal ions.

The reaction of Himp with copper(II) nitrate yields a green crystalline compound of which the X-ray structure is reported here, together with relevant spectral and magnetic properties.

Experimental

General

C, H, N and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland. IR spectra were recorded with KBr pellets in the range 4000–180 cm^{-1} on a Perkin-Elmer 580B spectrophotometer equipped with a Perkin-Elmer data station. UV–Vis spectra were obtained on a Perkin-Elmer 330 spectrophotometer using the diffuse reflec-

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tance technique, with MgO as a reference. X-band EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer. Mass spectroscopy was carried out on a Kratos MS9/50 spectrometer. Magnetic susceptibilities were measured in the temperature range 6.5–280 K with a fully automized Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at *c*. 1.4 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Synthesis of N,N'-imidopicolinyloxamylhydrazine

The ligand Himp was synthesized starting from commercially available 2-cyanopyridine and oxamic acid hydrazide as summarized in Scheme 1. 2-Cyanopyridine (0.2 mol; 20.8 g) was reacted with a solution of sodium (0.46 g) in 200 ml dry methanol to yield the methyl ester of imidopicolinic acid. After addition of 0.2 mol(20.6 g) of solid oxamic acid hydrazide the solution was refluxed for 2 h. Then the solution was filtered to remove non-reacted, undissolved oxamic acid hydrazide. From the filtrate the ligand Himp precipitated as a white solid. Melting point = ⩾250 °C. Mass spectrum: MW = 207. $(M+\mathrm{H})^+ = 208$, 190, 163, 122. IR spectroscopy: 3390 cm^{-1} (νN–H). *Anal.* Calc. for $C_8H_9N_5O_2$: C, 46.38; H, 4.35; N, 33.81. Found: C, 44.39; H, 4.39; N, 33.48%.

Synthesis of tetrakis[(N,N'-imidopicolinyloxamylhydrazine)copper(II)] tetranitrate octahydrate

The title compound $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$ was synthesized by mixing equimolar amounts (4 mmol; 0.82 g) of Himp and $Cu(NO_3)_2 \cdot 6H_2O$ (4 mmol; 0.92 g) in 50 ml of water. The resulting dark green solution was filtered. The compound crystallized upon evaporation of the solvent at room temperature after a few days. The dark green crystals were filtered, washed with water and dried in air. UV–Vis spectroscopy: asymmetric bond at 17.5×10^3 cm^{-1}. *Anal.* Calc. for $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$: C, 26.13; H, 3.29; N, 22.05; Cu, 17.28. Found: C, 26.26; H, 3.27; N, 22.85; Cu, 17.33%.

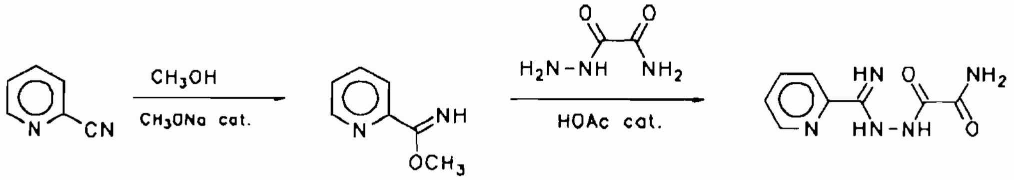
Crystal structure determination of $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$

A crystal of dimensions 0.2×0.2×0.3 mm was mounted in a Lindemann capillary. The cell constants were determined on a Enraf-Nonius CAD-4 automated diffractometer using Mo Kα radiation from 24 reflections with $6 < \theta < 8°$. A total of 1828 unique reflections was collected at room temperature. After data reduction, Lorentz and polarization corrections, the structure was solved with MULTAN 78 [8]. A planar CuN_3O chromophore was identified in the MULTAN solution, and, based on this, a complete model was obtained using DIRDIF [9]. Refinement of the structure with a local least-squares program lead to a final R value (unit weights) of 0.0639 ($R_w = 0.0700$), including 744 observed reflections for which $I > 2\sigma(I)$ and 95 parameters. After isotropic refinement of the complete model, empirical absorption corrections (computer program DIFABS [10]) were carried out. Apart from the metal ion all atoms were isotropic. The two hydrogen atoms of the water molecule were located in a difference Fourier map; the remaining hydrogen atoms were put in calculated positions (C–H = 1.00 Å) and positionally refined together with the corresponding non-hydrogen atoms. A unique common temperature factor was refined for all hydrogens. Parameters of data collection and refinements are given in Table 1. Final fractional coordinates for the non-hydrogen atoms are given in Table 2.

Results and discussion

Molecular structure of $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$

The coordination mode of the imp ligand is shown in Fig. 1, whereas the molecular structure of the chiral tetranuclear unit is depicted in Fig. 2. Relevant bond length and bond angle information is given in Table 3. The cluster consists of four copper(II) ions at the vertices of a flattened tetrahedron. Each copper(II) ion is coordinated by four donor atoms originating from two dehydronated ligands, thereby forming a distorted square planar CuN_3O chromophore. The deviations from the least-squares plane (Cu, N1, N2, N4, O2) are −0.066(6), −0.212(7), 0.224(6), −0.182(6) and 0.236(6) Å, respectively. The distances to the coordinating ni-



Scheme 1. Reaction scheme for the synthesis of Himp.

TABLE 1. Crystal and diffraction data for $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$

Chemical formula	$C_{32}H_{48}N_{24}O_{28}Cu_4$
M_r	1471.1
Crystal system	tetragonal
Space group	$I4_1/a$
$a=b$ (Å)	19.334(4)
c (Å)	15.257(13)
$\alpha=\beta=\gamma$ (°)	90
V (Å^3)	5703
Z (tetranuclear units)	4
T (K)	298
$F(000)$ (electrons)	2992
ρ_{obs} (g cm^{-3})	1.70
ρ_{calc} (g cm^{-3})	1.71
λ(Mo Kα) (Å)	0.71073
μ (cm^{-1})	15.76
Scan type	$\omega/2\theta$
2θ min.–max. (°)	2.0–22.0
Total no. data	2856
Observed data $[I>2\sigma(I)]$	744
No. refined parameters	95
R	0.0639
R_w	0.0700
GOF	1.418
Min. and max. residual density (e/Å^3)	−1.172, 1.708

$R=(\Sigma(|F_{obs}|-|F_{calc}|)/\Sigma|F_{obs}|)$. $R_w=[\Sigma w(|F_{obs}|-|F_{calc}|)^2/\Sigma w|F_{obs}|^2]^{1/2}$. $GOF=[\Sigma w(k|F_{obs}|-|F_{calc}|)^2/(NO-NV)]^{1/2}$.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å^2; $\times 10^2$ for Cu and O13; $\times 10$ for the other atoms) for the non-hydrogen atoms of $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$

Atom	x/a	y/b	z/c	U_{eq}[a]
Cu	5049(1)	1613(1)	7526(1)	152(5)
N1	4333(7)	1297(7)	6717(9)	17(2)
C1	4452(9)	1194(9)	5854(10)	21(3)
C2	3910(10)	911(10)	5358(14)	34(4)
C3	3282(10)	715(10)	5718(12)	28(4)
C4	3180(9)	840(9)	6601(11)	23(3)
C5	3729(9)	1130(8)	7082(10)	13(3)
C6	3699(9)	1265(9)	8048(10)	17(3)
N3	3152(7)	1109(8)	8515(9)	21(2)
N2	4278(7)	1541(6)	8341(9)	10(2)
N4	5861(7)	1816(6)	8238(8)	9(2)
C7	6401(9)	2034(9)	7804(10)	18(3)
O1	6986(6)	2161(6)	8104(8)	26(2)
C8	6246(8)	2092(8)	6825(10)	12(3)
N5	6755(7)	2334(8)	6339(10)	25(3)
O2	5642(6)	1948(6)	6571(7)	19(2)
N11	795(1)	118(1)	412(1)	49(4)
O11	8137(7)	693(8)	4599(9)	44(3)
O12	790(1)	177(1)	449(1)	84(5)
O13	787(1)	103(1)	337(2)	114(7)
O21	6663(7)	2410(7)	4398(9)	44(3)
O22	8633(11)	1645(10)	1897(12)	84(5)

[a] $U_{eq}=(U_{11}+U_{22}+U_{33})/3$.

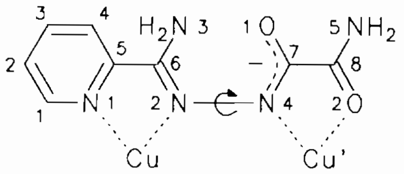


Fig. 1. The atomic numbering and the coordination mode of imp in $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$.

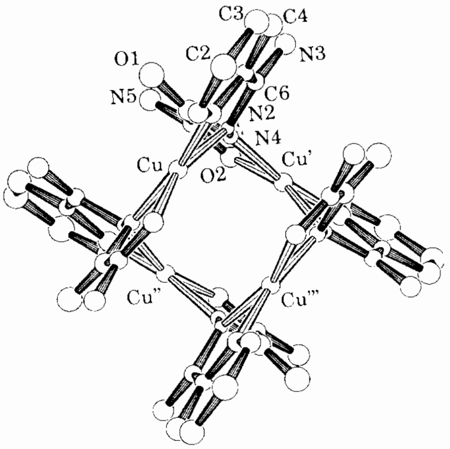


Fig. 2. The structure and the atomic labeling of the $[Cu(C_8H_8N_5O_2)]_4^{4+}$ cation. Atoms marked ′, ″ or ‴ are generated by symmetry operations: ′ = 0.75 − y, −0.25 + x, 1.75 − z; ″ = 0.25 + y, 0.75 − x, 1.75 − z; ‴ = 1 − x, 0.5 − y, z.

trogen atoms are all 1.95(1) Å; the distance to the coordinating oxygen atom is 1.96(1) Å. Each copper(II) ion has a nitrate anion acting as a semi-coordinated ligand with a Cu–O12 distance of 2.81(2) Å. The structure determination made clear beyond doubt that the O2, and not N5, coordinates to Cu(II). This was shown from the temperature factors assigned to the possible donor atoms. The dehydronated ligand imp coordinates to Cu via its pyridine group and the N2 of the N–N bridge. The other half of the ligand is twisted by about 90° around the N2–N4 bond and binds to the second Cu′ ion using N4 and O2. The angle between the least-squares planes (Cu, N1, N2, N4, O2) around Cu and Cu′ is 90°, i.e. the equatorial planes of the copper(II) ions are orthogonal with respect to each other. The distance between Cu and Cu′ is long, 4.456(4) Å, whereas the distance from Cu to Cu‴ is only 3.435(4) Å, although no bridging ligand is involved in this case.

A related tetranuclear cluster has been reported by Prins and co-workers [6, 7]. In that compound the copper(II) ions are linked by the flat 3-(pyridin-2-yl)-5-(pyrazin-2-yl)-1,2,4-triazolato anion resulting in a rather symmetric tetramer. This can easily be seen from the distances between copper(II) ions, which are directly linked by ligand bridges (4.27 Å) and between copper(II) lacking the triazole bridges (4.32 Å).

TABLE 3. Relevant bond lengths (Å) and angles (°) for $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$

Cu–Cu′	4.456(4)	C4–C5	1.41(2)
Cu–Cu″	4.456(4)	C5–C6	1.50(2)
Cu–Cu‴	3.435(4)	C6–N3	1.31(2)
Cu–N1	1.95(1)	C6–N2	1.32(2)
Cu–N2	1.95(1)	N2–N4	1.42(2)
Cu–N4	1.95(1)	N4–C7	1.31(2)
Cu–O2	1.96(1)	C7–O1	1.24(2)
Cu–O12	2.81(2)	C7–C8	1.53(2)
N1–C1	1.35(2)	C8–N5	1.32(2)
N1–C5	1.33(2)	C8–O2	1.26(2)
C1–C2	1.40(2)	N11–O11	1.24(2)
C2–C3	1.39(2)	N11–O12	1.28(2)
C3–C4	1.38(2)	N11–O13	1.20(2)
N1–Cu–N2	80.7(5)	N2–Cu–O2	160.9(5)
N1–Cu–N4	170.5(6)	N2–Cu–O12	119.1(6)
N1–Cu–O2	92.8(5)	N4–Cu–O2	82.9(5)
N1–Cu–O12	83.7(6)	N4–Cu–O12	87.1(5)
N2–Cu–N4	106.0(5)	O2–Cu–O12	77.6(6)
Cu–N1–C1	123(1)	N2–C6–C5	112(2)
Cu–N1–C5	116(1)	N2–C6–N3	126(2)
Cu–N2–C6	118(1)	N3–C6–C5	122(2)
Cu–N2–N4	126(1)	C6–N2–N4	116(1)
Cu–N4–N2	130(1)	N2–N4–C7	114(1)
Cu–N4–C7	115(1)	N4–C7–O1	127(2)
Cu–O2–C8	112.7(9)	N4–C7–C8	111(1)
C5–N1–C1	121(2)	O1–C7–C8	122(2)
N1–C1–C2	117(2)	C7–C8–N5	115(2)
C1–C2–C3	123(2)	O2–C8–C7	118(1)
C2–C3–C4	118(2)	O2–C8–N5	127(1)
C3–C4–C5	118(2)	O11–N11–O12	116(2)
C4–C5–N1	123(2)	O11–N11–O13	115(2)
N1–C5–C6	114(2)	O12–N11–O13	129(3)
C4–C5–C6	124(2)		

Atoms marked ′, ″ or ‴ are generated by symmetry operations: ′ = 0.75 − y, −0.25 + x, 1.75 − z; ″ = 0.25 + y, 0.75 − x, 1.75 − z; ‴ = 1 − x, 0.5 − y, z.

It appears that the plane of the pyridyl chelate part is more or less perpendicular to the plane of the oxamic acid part, i.e. 87.4(5)°. This probably is the driving force for the formation of a tetranuclear cluster of this type, the favoured conformation of the ligand being the one that has been found in the structure of the cluster. A dinuclear copper(II) coordination compound with bis(2-pyridylmethyl)ketazine shows a coordination mode similar to the one found for the imp ligand, although the twisting angle around the central N–N bond in that case is only 70.8° [11]. Recently, a dinuclear copper(II) compound with the ligand pyridoyl-2′-pyridinecarbohydrazide has been reported in which the twist angle is 170.8° [12].

In fact, the S_4 symmetry of the cluster results in a geometry in which the least-squares planes through the equatorial coordination spheres around Cu and Cu‴ are fairly parallel at roughly the Cu–Cu‴ distance of 3.435(4) Å.

The space group of this compound is $I4_1/a$ and the unit cell consists of four tetranuclear clusters with a center of symmetry lying between these clusters. This implies that in this unit cell two pairs of different enantiomers of the tetranuclear copper(II) clusters are present, as can be seen from Fig. 3.

The crystal structure determination did not allow distinction to be made between the different tautomeric structures of the anionic ligand. Taking into account that the hydrogens cannot be located on the coordinating atoms, and considering the distances C8–O2 and C8–N5, which are 1.26(2) and 1.32(2) Å, respectively, to be typical for acylic C=O groups [13, 14], it is easy to see that the four hydrogens are to be positioned on N3 and N5 as depicted in Fig. 1. The same tautomeric structure was found in a coordination compound of a similar acylamidrazone ligand in which the two hydrogens of N3 were positively found by difference Fourier calculations [15].

The crystal lattice contains several intermolecular and intramolecular H bonds between H_2O, NO_3 and the ligand imp (see Table 4).

Magnetic measurements

The magnetic susceptibility measurements (6.5–280 K) indicate that there is no significant magnetic interaction between the metal ions. This behaviour can be understood by examining the possible exchange pathways. Because of the orthogonality of the $d(x^2-y^2)$ orbitals on two nearest neighbour copper(II) ions a ferromagnetic interaction between the pairs of metal ions, (Cu, Cu′) and (Cu, Cu″), is predicted [16]. Noting that these metal ions are only linked by a single diatomic bridge and have a Cu–Cu′ distance of 4.456(4) Å, no significant magnetic interaction is expected. Between Cu and Cu‴ an exchange pathway would principally

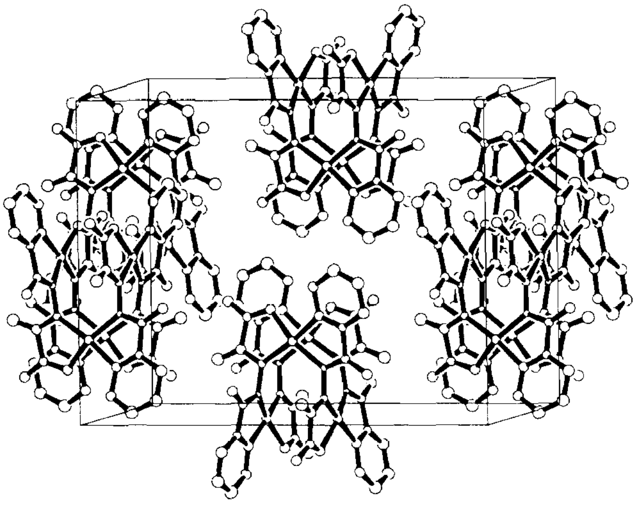


Fig. 3. Projection of the unit-cell contents of $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$.

TABLE 4. Interatomic distances (Å) and angles (°) for the hydrogen bonding interactions in $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$

O13···O22	2.93(3)	H222···O13	2.70(3)	O13–H222···O22	96.3(7)
O21···O22^1	2.92(2)	H221^1···O21	2.14(2)	O21–H221^1···O22^1	145.6(7)
N3···O11^2	2.99(2)				
N3···O11^3	2.91(2)				
N5···O21	2.97(2)				
O21···O22^4	2.75(2)				
O1···N5	2.75(2)				
O1–N5^5	2.76(2)				

Atoms marked with a number are generated by symmetry operations: $1=0.75-y,\ -0.75+x,\ 0.25+z$; $2=-0.50+x,\ y,\ 1.50-z$; $3=0.25-y,\ -0.75+x,\ 1.25-z$; $4=1.50-x,\ 0.50-y,\ 0.50-z$; $5=1.5-x,\ 0.5-y,\ 1.5-z$.

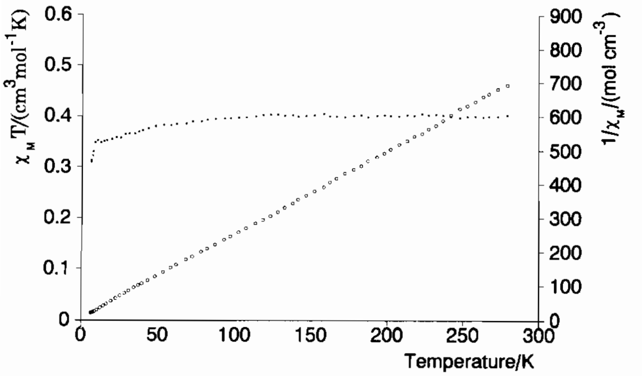


Fig. 4. $1/\chi$ vs. T (○) and χT vs. T (■) curves for $[Cu(C_8H_8N_5O_2)]_4(NO_3)_4(H_2O)_8$.

be possible, because here the d(x^2–y^2) orbitals situated on these copper(II) ions are parallel. But since no bridging ligand is involved the antiferromagnetic interaction arising from this exchange pathway would necessarily be negligible. As a net result from both possible exchange pathways a negligible magnetic interaction is expected, which is indeed confirmed by the magnetic susceptibility measurements recorded in the 6.5–280 K temperature region (see Fig. 4). At 280 K the product of the magnetic susceptibility (χ) and the temperature (T) is 0.400 cm^3 mol^{-1} K, which fits very well with the theoretical value for isolated $S=1/2$ ions. When the temperature is lowered the value of χT goes down to a value of 0.313 cm^3 mol^{-1} K at 6.5 K, indicating that there is a very small antiferromagnetic interaction taking place.

The X-band powder EPR spectra at 298 and 77 K show an isotropic signal around $g=2.09$, i.e. what would be expected for copper(II) ions having no magnetic interaction.

Conclusions

By comparing chelating 1,2,4-triazole ligands with their non-cyclized precursors, it can be concluded that acylamidrazones possess a larger flexibility in coordination by rotation around the N–N bond.

This new tetranuclear copper(II) compound also shows that in spite of the relatively short distances between neighbouring copper(II) ions a negligible magnetic interaction is found, due to the orthogonality of the magnetic orbitals.

Supplementary material

Tables of anisotropic thermal parameters, positional and thermal parameters for hydrogen atoms, selected least-squares planes, and a table of calculated and observed structure factors may be obtained from the authors.

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