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Crystal Structure of μ-Peroxo-bis[nitrobis(ethylenediamine)-cobalt(III)] Dinitrate Tetrahydrate[1)]

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The crystal and molecular structure of μ-peroxo-bis[nitrobis(ethylenediamine)cobalt(III)] dinitrate tetrahydrate, $[NO_2(en)_2CoO_2Co(en)_2NO_2](NO_3)_2\cdot 4H_2O$ has been determined using visual intensity data of three dimensional Weissenberg photographs taken with Ni-$K\alpha$ radiation. The brown-black salt is monoclinic with space group $P2_1/n$ and cell dimensions $a=10.755\pm0.011$, $b=12.941\pm0.008$, $c=9.709\pm0.006$ Å, and $\beta=100.4\pm0.1°$. The least-squares refinement with anisotropic temperature factors gave an R index of 0.106. The coordinating ligands form nearly regular octahedra about the cobalt atoms, with Co–N(en), Co–N(NO_2), and Co–O distances of about 1.95, 1.94, and 1.89 Å, respectively. Both NO_2^-'s are *trans* to the O–O bridge, and the geometry of Co–O–O–Co is *trans* planar with O–O distance of 1.53 Å and Co–O–O angle of 110°. The two Co–$(en)_2$ moieties have $\delta\delta$ and $\lambda\lambda$ conformations.

It is well-known that a cobalt-ammonia solution takes up molecular oxygen in aqueous solution to give a brown diamagnetic decaammine μ-peroxo dicobalt complex, which can be oxidized further by Cl_2, $KMnO_4$, *etc.* to yield a green paramagnetic decaammine μ-superoxo dicobalt complex. Several instances of X-ray analyses of decaammine μ-O_2 (both peroxo and superoxo) dicobalt complexes $[(NH_3)_5CoO_2Co(NH_3)_5]^{n+}$

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(n=4, 5) have been reported.[2–5] The O–O distances were reported to be 1.31—1.32 Å for superoxo complexes; the O–O distance in KO_2 is 1.28 Å. For peroxo complexes, Schaefer reported 1.47 Å,[5] although Vannerberg had given a considerably longer O–O distance (1.65 Å).[4] Recently we found that $[NH_3(en)_2CoO_2Co(en)_2NH_3]^{4+}$ reacts with NO_2^- in a neutral solution to give $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ without causing any cleavage of the O_2-bridge.[6] The present report deals with the crystal and molecular structure of this new complex. This seems to be the first example of an O_2-single-bridged dicobalt complex with coordinated nitro groups as studied by X-ray analysis.

Studies have been carried out on the *cis-trans* problem of a mononuclear complex, but very little is known about *cis-trans* configuration in binuclear complexes, partly because most of the binuclear dicobalt complexes so far determined by X-ray analyses were of the unsubstituted ammine type. It seemed worthwhile to investigate the geometrical isomerism of binuclear complexes.

Experimental

Crystals of μ-peroxo-bis[nitrobis(ethylenediamine)cobalt(III)] dinitrate tetrahydrate recrystallized from an aqueous solution are monoclinic brown-black prisms. The compound is stable against air oxidation. Cell dimensions were obtained from zero-level Weissenberg films, taken about the a and b axes, on which the diffraction pattern of silicon powder (a= 5.43066 Å) was superimposed for calibration. The space group $P2_1/n$ was indicated on Weissenberg photographs by a systematic absence of reflections $h0l$ with $h+l$ odd and $0k0$ with k odd. The density of the compound was determined by flotation in a chloroform–bromoform mixture. The crystal data are listed in Table 1. The intensities were measured visually on integrated multi-film equiinclination Weissenberg photographs taken with Ni-$K\alpha$ radiation, for layers from $0kl$ through $7kl$ and from $h0l$ through $h8l$. The intensities were corrected for Lorentz, polarization and absorption factors. In all, 2331 independent (1994 non-zero) reflections were obtained.

TABLE 1. CRYSTAL DATA

$[NO_2(en)_2CoO_2Co(en)_2NO_2](NO_3)_2\cdot 4H_2O$
Monoclinic
$a=10.755\pm0.011$, $b=12.941\pm0.008$, $c=9.709\pm0.006$Å
$\beta=100.4\pm0.1°$
$D_m=1.70$ g cm^{-3} $D_c=1.70$ g cm^{-3}
$Z=2$, space group $P2_1/n$
Linear absorption coefficient for Ni-$K\alpha$ radiation,
$\mu=28.39$ cm^{-1}

Structure Determination

Approximate coordinates of the cobalt atom were found from three-dimensional Patterson synthesis. The center of the μ-peroxo group lies on the crystallographic center of symmetry. A three dimensional electron density map was then calculated on the basis of cobalt contribution. R index $(\sum||F_o|-|F_c||/\sum|F_o|)$ was 0.435. Several cycles of Fourier and differential Fourier syntheses revealed all the non-hydrogen atoms. The atomic parameters and individual isotropic temperature factors were refined by three cycles of the block diagonal least-squares method. At this stage the R index was 0.154. Three more cycles of refinement were carried out on introduction of anisotropic temperature factors. The following weighting scheme was employed:

$$w = 0.15, \text{ if } F_o \leqq F_{min} (=4.04);$$

TABLE 2. ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATONS[a] ($\times 10^4$)
Temperature factors are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	1139(1)	1348(1)	1046(1)	57(1)	37(1)	66(1)	−9(2)	−6(2)	−5(2)
O(1)	171(5)	505(4)	−330(5)	39(5)	17(3)	30(6)	−31(6)	−10(8)	15(7)
O(2)	2198(10)	2101(9)	3667(8)	183(13)	132(10)	62(9)	−198(19)	−44(18)	−16(15)
O(3)	2718(9)	2989(7)	2073(9)	167(12)	62(6)	129(12)	−154(15)	55(19)	−72(14)
O(4)	1074(8)	1352(8)	−3268(8)	116(10)	167(9)	72(9)	67(16)	7(15)	16(15)
O(5)	639(11)	2978(11)	−3277(18)	146(14)	143(13)	472(35)	51(22)	−99(37)	−419(37)
O(6)	−300(7)	2011(7)	−4904(8)	81(8)	86(7)	68(8)	45(12)	−33(13)	−33(12)
O(7)	1700(8)	−129(7)	4864(8)	110(9)	62(6)	110(10)	15(12)	65(16)	28(12)
O(8)	861(14)	4412(14)	−780(23)	200(18)	203(19)	616(50)	−252(30)	−310(51)	506(52)
N(1)	2314(7)	1582(5)	−231(8)	51(7)	21(4)	65(8)	−9(9)	2(12)	8(9)
N(2)	2150(6)	164(6)	1740(7)	32(6)	32(5)	47(7)	3(9)	−2(11)	14(9)
N(3)	−77(6)	1074(6)	2272(7)	38(6)	31(5)	47(7)	−6(9)	3(11)	−8(9)
N(4)	45(7)	2511(5)	328(7)	49(6)	25(4)	62(8)	6(9)	−17(12)	−9(10)
N(5)	2133(7)	2241(6)	2430(8)	57(7)	42(5)	53(8)	−2(10)	−12(13)	10(11)
N(6)	486(8)	2133(8)	−3816(10)	49(7)	85(8)	103(11)	35(13)	26(15)	−68(16)
C(1)	3109(9)	617(8)	−267(11)	56(9)	47(7)	109(13)	10(13)	62(18)	20(15)
C(2)	3392(9)	186(9)	1237(12)	42(8)	55(8)	131(15)	17(13)	29(18)	60(17)
C(3)	−1220(9)	1751(8)	1841(10)	46(8)	47(6)	75(11)	1(12)	21(15)	−26(14)
C(4)	−738(9)	2782(8)	1360(10)	61(9)	39(6)	78(11)	19(12)	4(16)	−27(13)

a) Standard deviations of least significant figures are given in parentheses.

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2) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 735 (1966).

3) R. E. Marsh and W. P. Schaefer, *ibid.*, **B24**, 246 (1968).

4) N. G. Vannerberg, *ibid.*, **18**, 449 (1965).

5) W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).

6) T. Shibahara and M. Mori, This Bulletin, **45**, 1433 (1972).

7) International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham (1962), p. 202.

Table 3. Calculated hydrogen atom positions[a] ($\times 10^4$)

Atom		x/a	y/b	z/c
N(1)	H(1)	2818	2122	66
	H(2)	1883	1719	−1095
N(2)	H(3)	1730	−418	1433
	H(4)	2292	168	2682
N(3)	H(5)	279	1210	3166
	H(6)	−309	405	2204
N(4)	H(7)	−452	2332	−485
	H(8)	520	3058	178
C(1)	H(9)	3910	790	−595
	H(10)	2630	95	−917
C(2)	H(11)	3755	−526	1243
	H(12)	4007	642	185
C(3)	H(13)	−1662	1864	2650
	H(14)	−1821	1422	1058
C(4)	H(15)	−1462	3229	927
	H(16)	−227	3158	2169

a) All hydrogen atoms were assigned isotropic temperature factors, $B=3.5$ Å^2.

$$w = 1.0, \quad \text{if } F_{\text{min}} < F_o < F_{\text{max}} \ (=30.7);$$
$$w = F_{\text{max}}/F_o, \quad \text{if } F_o > F_{\text{max}}$$

The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[7] The R index was 0.113 for all the observed reflections. The positions of fourteen hydrogen atoms attached to ethylenediamine molecules were apparent from difference maps, but residual two hydrogen-atom positions were obscure. Although least-squares refinement including hydrogens gave R of 0.103, it indicated some unreasonable short C–H and N–H distances. Thus, neither their coordinates nor their temperature factors were refined. Instead, the hydrogen-atom positions were calculated assuming a tetrahedral configuration about the carbon and nitrogen atoms in ethylenediamine molecules, and C–H and N–H distances of 1.00 and 0.90 Å.[5,8] Inclusion of these assumed hydrogen positions gave R index of 0.106.

The final atomic coordinates and anisotropic temperature factors of the form: $\exp(-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl))$ together with their estimated standard deviations are given in Table 2, and the calculated hydrogen-atom parameters in Table 3. A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan.[9]

Description and Discussion of Structure

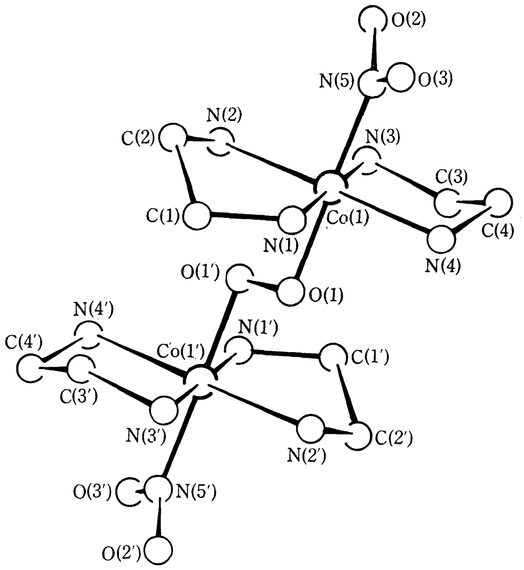

Fig. 1. Perspective drawing of $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ cation.

Table 4. Interatomic distances within the ions

Distance	Value, Å	Distance	Value, Å
Co(1)–O(1)	1.887(6)	N(5)–N(1)	2.761(11)
–N(1)	1.947(8)	–N(2)	2.772(11)
–N(2)	1.927(7)	–N(3)	2.796(11)
–N(3)	1.953(7)	–N(4)	2.770(11)
–N(4)	1.960(7)	O(1)–N(1)	2.681(9)
–N(5)	1.940(8)	–N(2)	2.687(9)
N(5)–O(2)	1.204(14)	–N(3)	2.691(9)
–O(3)	1.238(13)	–N(4)	2.684(9)
O(1)–O(1')	1.529(9)	O(1')–N(1)	3.907(9)
N(1)–C(1)	1.515(13)	–N(2)	2.756(9)
N(2)–C(2)	1.503(14)	–N(3)	2.769(9)
N(3)–C(3)	1.507(13)	–N(4)	3.910(9)
N(4)–C(4)	1.462(12)	N(6)–O(4)	1.258(15)
C(1)–C(2)	1.542(16)	–O(5)	1.211(21)
C(3)–C(4)	1.534(14)	–O(6)	1.238(14)

A perspective drawing of the complex cation is given in Fig. 1, and the atomic arrangement in the crystal in projection along the b axis in Fig. 2. Interatomic distances and bond angles within the ions are listed, along with their estimated standard deviations, in Tables 4 and 5. Each cobalt atom is surrounded octahedrally by four nitrogen atoms of ethylenediamine molecules, a nitrogen atom of the nitro group, and an oxygen atom of the bridging group. As the center of the μ-peroxo group lies on the crystallographic center of symmetry, the geometry of Co–O–O–Co is *trans* coplanar. The torsion angle (180°) about the O–O bond is thus much larger than 146° found for the decaammine μ-peroxo dicobalt (4+) cation reported by Schaefer.[5] This is probably due to the greater steric hindrance between coordinated ethylenediamine groups across the bridge than that between coordinated ammine groups. The short distances across the bridge are those of C(1)···C(3′) and C(3)···C(1′), and are both 3.83 Å, *i.e.* less than twice the van der Waals radius (2.0 Å) of C–H. The nitro ligand has *trans* configuration to the μ-peroxo bridge. The O–O distance in the bridge is 1.53 Å, somewhat longer than that found in H_2O_2 (1.47—1.49 Å)[10,11] and BaO_2

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[8] D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg, Chem.*. **10**, 1061 (1971).

[9] The complete data of the Fo—Fc table are kept as Document No. 7312 at the office of the Bulletin of the Chemical Society of Japan.

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[11] S. C. Abrahams, R. L. Collin, and W. N. Lipscomb, *Acta Crystallogr.*, **4**, 15 (1951).

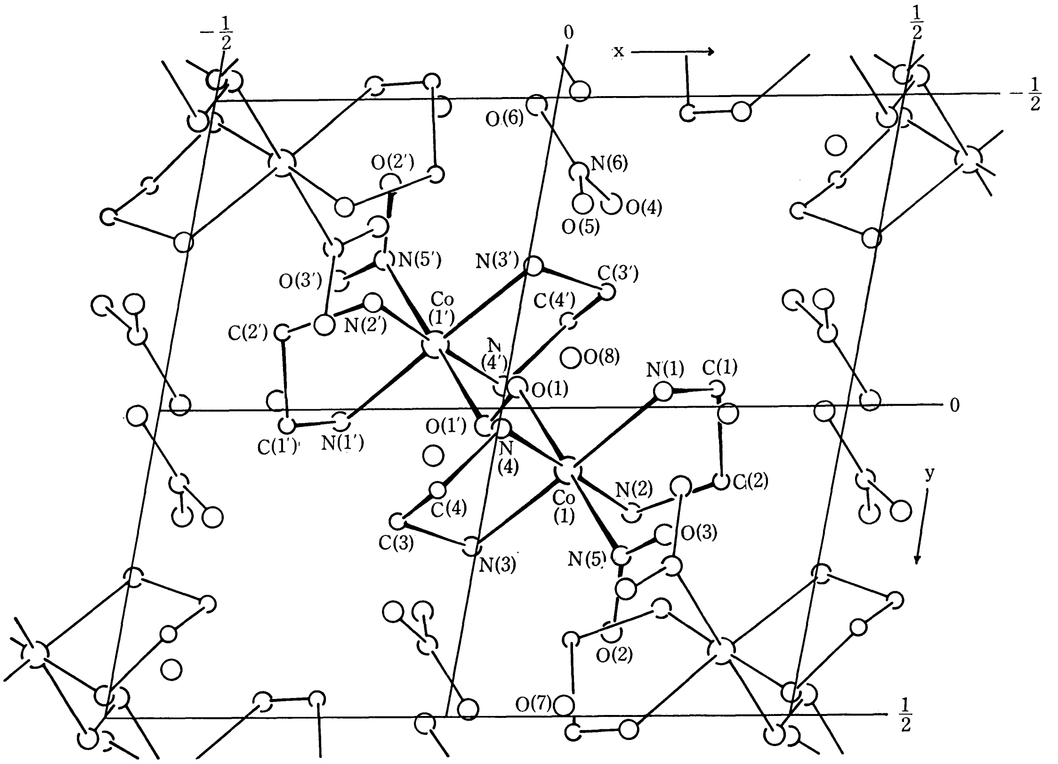

Fig. 2. The atomic arrangement in projection along the b axis.

Table 5. Bond angles

Angle	Deg.	Angle	Deg.
Co(1)-O(1)-O(1')	110.0(6)	Co(1)-N(1)-C(1)	108.6(6)
O(1)-Co(1)-N(1)	88.7(3)	Co(1)-N(2)-C(2)	110.4(6)
O(1)-Co(1)-N(2)	89.5(3)	Co(1)-N(3)-C(3)	109.1(6)
O(1)-Co(1)-N(3)	89.0(3)	Co(1)-N(4)-C(4)	108.9(6)
O(1)-Co(1)-N(4)	88.5(3)	N(1)-C(1)-C(2)	107.1(8)
N(1)-Co(1)-N(2)	87.5(3)	N(2)-C(2)-C(1)	106.1(9)
N(3)-Co(1)-N(4)	86.1(3)	N(3)-C(3)-C(4)	106.7(8)
N(1)-Co(1)-N(4)	94.1(3)	N(4)-C(4)-C(3)	105.5(8)
N(2)-Co(1)-N(3)	92.3(3)	O(1)-Co(1)-N(5)	178.7(3)
Co(1)-N(5)-O(2)	121.8(8)	N(1)-Co(1)-N(3)	177.6(3)
Co(1)-N(5)-O(3)	121.1(7)	N(2)-Co(1)-N(4)	177.4(3)
O(2)-N(5)-O(3)	117.1(10)	O(4)-N(6)-O(5)	121.6(13)
N(5)-Co(1)-N(1)	90.5(3)	O(5)-N(6)-O(6)	120.2(13)
N(5)-Co(1)-N(2)	91.5(3)	O(6)-N(6)-O(4)	118.1(10)
N(5)-Co(1)-N(3)	91.8(3)		
N(5)-Co(1)-N(4)	90.5(3)		

(1.49 Å).[12] The Co–O distance is 1.89 Å about the same as that found in the μ-O_2 decaammine (both superoxo and peroxo) complexes. The Co–N(NO_2) distance is 1.940(8) Å, essentially the same as the value 1.92(2) Å in $[CoNO_2(NH_3)_5]Br_2$.[13] Thus, there appeares no significant structural *trans* effect of the O_2 and NO_2 groups. This is in agreement with the fact that $[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$ is stable in an aqueous solution. The Co–O–O angle is 110°, somewhat smaller than that reported for the μ-O_2 compound. An average of 1.947(8) Å was obtained for the four Co–N(en) distances, comparable with Co(III)–N(sp^3) distances given in literature such as $[(NH_3)_5CoO_2Co(NH_3)_5](SO_4)_2\cdot 4H_2O$, 1.962(9) Å; *trans* $[CoCl(NO)(en)_2]ClO_4$,[14] 1.964(5) Å; and $[Co(NH_3)_6]I_3$,[15] 1.936 (15) Å.

The Co–$(en)_2$ moieties have unusual $\delta\delta$ and $\lambda\lambda$ con-

Table 6. Puckering of the ethylenediamine rings

Plane defined by atoms	Atom	Deviation from plane, Å
Co(1), N(1), N(2)	C(1)	−0.36
	C(2)	0.32
Co(1), N(3), N(4)	C(3)	−0.26
	C(4)	0.49

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[12] S. C. Abrahams and H. A. Levy, *J. Chem. Phys.*, **7**, 838 (1954).

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[15] N. E. Kime and J. A. Ibers, *Acta Crystallogr.*, **B25**, 168 (1969).

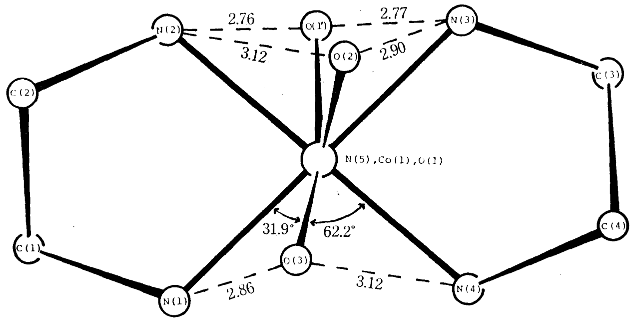

Fig. 3. The view of half of the cation along the N(5), Co(1), O(1) bonds.

figurations. The out-of-plane distances in relation to the puckering of the ethylenediamine rings are listed in Table 6. All *trans* bis(ethylenediamine) complexes so far determined by X-ray analyses have $\delta\lambda$ conformation[16,17] except for $[CoCl(NO)(en)_2]ClO_4$. As is shown in Fig. 3, the NO_2 plane does not bisect the N(1)–Co(1)–N(4) angle, in contrast to $[CoNO_2(NH_3)_5]$-Br_2, and O(3)–N(1) and O(2)–N(3) have rather short distances 2.86 and 2.90 Å, respectively, implying hydrogen bonding. Existence of hydrogen bonding can also be inferred between O(1′) and N(2) (2.76 Å) as well as between O(1′) and N(3) (2.77 Å). The two sp^3-type unshared electron orbitals of bridging oxygen O(1′) should point toward the vicinity of hydrogen atoms attached to N(2) and N(3) atoms. These may be partly respondible to the $\delta\delta$ and $\lambda\lambda$ configurations of the complex ion. The possible hydrogen bondings with N-H···O distances less than 3.3 Å and O-H···O distances less than 3.0 Å are listed in Table 7. It is interesting that both the first example of $\delta\delta$ and $\lambda\lambda$ configuration ($[CoCl(NO)(en)_2]^+$) and the present one ($[NO_2(en)_2CoO_2Co(en)_2NO_2]^{2+}$) have rather abnormal ligands such as –NO or –O–O– considered to give some specific π-bonding character. The nitro group is planar within experimental error, with N–O distances of 1.21—1.26 Å and O–N–O angles of 118.1—121.6°. The short distances between N(4)–O(8), O(8)–O(7), O(7)–O(4), and O(7)–O(6) appear to be due to intermolecular hydrogen bonds. Cations and anions alternately form layers parallel to the plane $(\bar{1}01)$.

TABLE 7. POSSIBLE HYDROGEN BONDINGS[a)]

From	To	Distance, Å
N(1)	O(3), a	2.86
	O(4), a	3.02
	O(6), d	3.12
N(2)	O(1′), a	2.76
	O(7), a	3.18
N(3)	O(1′), a	2.77
	O(2), a	2.89
	O(6), a	3.05
N(4)	O(8), a	2.89
O(4)	O(7), a	2.80
O(6)	O(7), b	2.87
O(7)	O(8), c	2.68

a) The translations are as follows:
(a) x, y, z; (b) $-x, -y, -z$;
(c) $-x, +y, -z$; (d) $+x, -y, +z$.

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