Table II. Experimental Data for the X-ray Diffraction Study of $[Tc(THMT)_2]$

formula	$C_{28}H_{66}I_2N_4O_{12}{}^{99}Tc_2$	ρ_{calcd}, g cm^{-3}	3.32
mol wt	1101.64	μ, cm^{-1}	40.96
space group	$C2/c$ (No. 15)	T, °C	22
a, Å	28.334 (5)	λ, Å	0.71069 (graphite monochromated, Mo Kα)
b, Å	10.199 (2)		
c, Å	15.196 (2)		
β, deg	116.74 (1)	transm coeff	0.897–0.999
Z	4	R	0.055
V, Å^3	3921.7	R_w	0.064

Table III. Final Atomic Coordinates and Equivalent Thermal Parameters with Esd's in Parentheses[a]

atom	x	y	z	B, Å^2
I1	0.74611 (3)	−0.0275 (1)	0.36429 (6)	5.12 (3)
TC1	0.000	0.000	0.000	1.67 (2)
O1	0.0727 (2)	0.0680 (7)	0.0411 (4)	3.3 (1)
O2	0.0018 (2)	0.0930 (6)	0.1179 (4)	3.3 (1)
O3	0.0332 (2)	−0.1520 (6)	0.0897 (4)	3.3 (1)
O4[b]	−0.0728 (2)	0.2711 (7)	0.0831 (5)	4.5 (2)
O5[b]	−0.1411 (3)	0.6180 (7)	0.1307 (5)	5.3 (2)
O6[b]	−0.0196 (3)	0.6336 (8)	0.0434 (6)	7.0 (2)
N1	0.1376 (2)	0.0079 (7)	0.3132 (5)	3.0 (2)
N2	−0.1268 (3)	0.5049 (8)	−0.0407 (5)	3.5 (2)
C11	0.1128 (3)	0.020 (1)	0.1295 (6)	3.6 (2)
C22	0.0529 (3)	0.1228 (9)	0.1948 (7)	3.7 (2)
C33	0.0614 (4)	−0.1267 (9)	0.1921 (6)	3.7 (2)
C101	0.0910 (3)	0.0051 (9)	0.2088 (5)	2.8 (2)
C102	0.1200 (4)	−0.037 (1)	0.3897 (6)	3.9 (2)
C103	0.1597 (4)	0.1467 (9)	0.3430 (7)	4.3 (3)
C104	0.1829 (4)	−0.081 (1)	0.3208 (7)	3.9 (2)
C44[b]	−0.0457 (3)	0.3913 (9)	0.0944 (7)	3.5 (2)
C201[b]	−0.0845 (3)	0.508 (1)	0.0686 (6)	3.2 (2)
C202[b]	−0.1499 (5)	0.640 (1)	−0.0796 (9)	6.7 (4)
C203[b]	−0.1033 (4)	0.452 (1)	−0.1072 (7)	5.9 (3)
C204[b]	−0.1725 (4)	0.414 (1)	−0.058 (1)	5.9 (3)
C55[b]	−0.1107 (3)	0.500 (1)	0.1390 (7)	4.1 (2)
C66[b]	−0.0517 (4)	0.637 (1)	0.0936 (7)	4.6 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2B(1,1) + b^2(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] Atoms of the $[H_3THMT]^+$ counterion; for the numbering scheme see the suplementary diagram.

mmol) and 1.02 g of **3** (3.5 mmol) under an argon atmosphere, and the mixture was treated in an ultrasonic vibrator. The color of the solution changed to red brown. After all of the $Bu_4N[TcOCl_4]$ had dissolved, the solution was controlled by using paper chromatography (Whatman CF-1; $CH_3CN:H_2O$ = 5:2 v/v). This showed the presence of $Tc(THMT)_2$ (65%, R_f = 0.3) and TcO_4^- (33%, R_f = 1) together with polymeric species (1–2%, R_f = 0).

Determination and Refinement of the Structure. Crystals suitable for X-ray diffraction of $[Tc(THMT)_2]\cdot 2(H_3THMT)I$ were obtained as described above and are air stable. A prismatic white crystal mounted on a glass fiber at a random orientation on an Enraf-Nonius CAD4 diffractometer was used for the unit cell and space group determination and for the data collection. Unit cell dimensions were obtained by a least-squares fit of the 2ϑ values of 25 high-order reflections ($9.5 < \vartheta < 17.0°$) using the CAD4 centering routines. Selected crystallographic and other relevant data are listed in Table II; an extended list of structural and data collection parameters is given in supplementary Table S1. Data were measured with a variable scan speed to ensure constant statistical precision on the collected intensities. Three standard reflections were used to check the stability of the crystal and of the experimental conditions and were measured every hour; no significant variation was detected. The orientation of the crystal was checked by measuring three reflections every 300 reflections. Data were corrected for Lorentz and polarization effects and for decay, by using the data reduction programs of the CAD4-SDP package.[10] An empirical absorption correction was also applied by using azimuthal (ψ) scans of three reflections at a high χ angle ($\chi \geq 84°$). Transmission factors were in the range 0.897–0.999. Intensities were considered as observed if $|F_o|^2 \geq 2.5\sigma|F|^2$. A F_o = 0.0 was assigned to those reflections having negative net intensities. The structure was solved by a combination of Patterson and Fourier methods and refined by full-matrix least squares[10] (the function minimized was $\sum[w(|F_o| - (1/k)|F_c|)^2]$ with $w = (\sigma^2|F_o|)^{-1}$). No extinction correction was deemed necessary. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from ref 11. Anisotropic temperature factors were used for all non-hydrogen atoms. Upon convergence (no parameter shift $>0.2\sigma(p)$), the final Fourier difference map showed no significant features. Final atomic coordinates and equivalent thermal factors are given in Table III.

Acknowledgment. Financial support from the Schweizerischer Nationalfond and Paul Scherrer Institut, Würenlingen (R.A and G.H), is gratefully acknowledged.

Registry No. K_2**1**, 98479-41-5; **4**, 135366-82-4; $Bu_4N[^{99}TcOCl_4]$, 92622-25-8.

Supplementary Material Available: A diagram showing the atom numbering of the $[H_3THMT]^+$ cation, a complete list of crystal data and experimental parameters (Table S1), a table of anisotropic displacement parameters (Table S2), and extended lists of bond lengths and bond angles (Tables S3 and S4) (6 pages); a list of observed and calculated structure factors (Table S5) (20 pages). Ordering information is given on any current masthead page.

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(10) Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, The Netherlands, 1980.

(11) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Contribution from the Department of Chemistry
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Low-Coordinate Yttrium in an Oxygen Ligand Environment. Solid-State and Solution Characterization of $Y_2(OSiPh_3)_6$

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and Kenneth G. Caulton*

Received February 13, 1991

We have reported[1] that treatment of $Y[N(SiMe_3)_2]_3$ with Ph_3SiOH in toluene gives a high yield of a material of empirical formula $Y(OSiPh_3)_3$. On the basis of its low solubility and its complex ^1H and ^{13}C NMR spectra, we have concluded that this is an aggregate. However, establishing the exact degree of aggregation was not possible, in part because we were only able to produce featherlike solids unsuitable for an X-ray structure determination. While this compound was shown to react with a variety of ligands to yield adducts of varying coordination numbers (eq 1–4), the detailed composition and structure of the reagent remained unknown.

$$[Y(OSiPh_3)_3]_n \xrightarrow{THF} fac\text{-}Y(OSiPh_3)_3(THF)_3 \qquad (1)$$

$$[Y[OSiPh_3)_3]_n \xrightarrow{py} fac\text{-}Y(OSiPh_3)(py)_3 \qquad (2)$$

$$[Y(OSiPh_3)_3]_n \xrightarrow{^nBu_3PO} Y(OSiPh_3)[OP^nBu_3]_2 \qquad (3)$$

$$[Y(OSiPh_3)_3]_n \xrightarrow{OSiPh_3^-} Y(OSiPh_3)_4^- \xrightarrow{MeOC_2H_4OMe} cis\text{-}Y(OSiPh_3)_4(MeOC_2H_4OMe)^- \qquad (4)$$

We report here the resolution of this uncertainty as well as an application of ^{29}Si NMR spectroscopy to evaluate solution structure. This NMR technique convincingly resolves bridging and terminal siloxide environments.

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(1) McGeary, M. J.; Coan, P. S.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.*, in press.

0020-1669/91/1330-3570$02.50/0

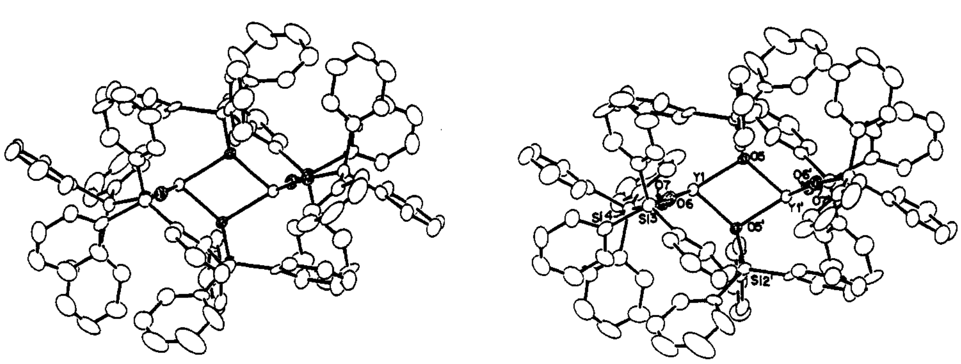


Figure 1. Stereo ORTEP drawing of the non-hydrogen atoms of $Y_2(OSiPh_3)_6$, showing selected atom labeling. Oxygens are stippled. Primes indicate atoms related by the crystallographic center of symmetry.

Table I. Crystallographic Data for $Y_2(OSiPh_3)_6$

formula	$C_{115}H_{98}O_6Si_6Y_2$	space group	$P2_1/n$
a, Å	14.258 (3)	T, °C	−129
b, Å	15.416 (3)	λ, Å	0.71069
c, Å	22.311 (5)	ρ_{calcd}, g cm^{-3}	1.302
β, deg	91.49 (1)	μ(Mo Kα), cm^{-1}	13.1
V, Å^3	4902.47	R	0.0810
Z	2	R_w	0.0658
fw	1922.36		

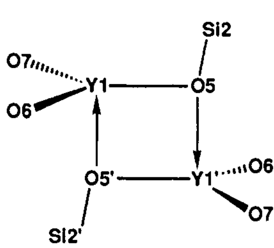
Experimental Section

NMR spectra, ^1H, ^{13}C, and ^{29}Si, were acquired on a Bruker AM-500 spectrometer operating at 500, 125.7, and 99.36 MHz, respectively. $CDCl_3$ was dried over P_2O_5 and then subjected to repeated freeze–pump–thaw cycles to remove dissolved gases. ^1H and ^{13}C NMR spectra were acquired in 5-mm sample tubes and ^{29}Si NMR spectra were obtained in 10-mm sample tubes by using an inverse gated decoupling routine.

X-ray Structure Determination. X-ray-quality crystals were obtained by dissolving $[Y(OSiPh_3)_3]_2$ in toluene (20 mL) to generate a saturated solution. Additional toluene (5 mL) was then added to dilute the solution. Hexanes (50 mL) were then carefully layered on the toluene solution. After 18 days, small cubes had formed. Repeated attempts to grow crystals by very slowly cooling a saturated solution of this complex in toluene yielded only featherlike crystals. A crystal was mounted with silicone grease and was transferred to a goniostat, where it was cooled to −129 °C for characterization and data collection ($6° < 2\theta < 45°$). A systematic search of a limited hemisphere of reciprocal space revealed symmetry and systematic absences corresponding to the monoclinic space group $P2_1/n$. Characteristics of the crystal are shown in Table I. No absorption correction was performed because of the irregular sample shape. The equidimensional character of the crystal minimizes the impact of this decision. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. The Y atom position was obtained from an initial E map, and the remainder of the non-hydrogen atoms were found in subsequent iterations of least-squares refinement and difference Fourier calculations. After partial refinement of the non-hydrogen atoms, a difference Fourier synthesis revealed some of the hydrogen atoms. All phenyl hydrogens were included in idealized (d(C–H) = 0.95 Å) positions. The crystal structure contains not only the rigorously centrosymmetric Y dimer but also a molecule of toluene. The solvent molecule lies on the center of symmetry, so its methyl group is statistically disordered.

Results

Solid-State Structure. The molecule is a dimer in the solid state and possesses a crystallographic center of symmetry (Figure 1). The dimeric structure resembles that of diborane and of Al_2Cl_6, but the differences from these edge-shared bitetrahedra are significant. The bridging Y–O distances (which are at least 0.15 Å longer than those to the terminal oxygens) are markedly (11σ) asymmetric. The shorter of these involves Y(1)–O(5). Atoms O(5), O(6), O(7), and Y(1) are coplanar (the angles around Y(1) sum to 359.1°). Such asymmetry is of course markedly different from a regular edge-shared bitetrahedron and leads to structure I as a limiting representation of the bonding. Atom O(5) is coplanar with its three attached groups, but Si(2) bends significantly toward the open side of the planar metal (i.e., toward the region trans to O(5)′); the angles Y(1)–O(5)–Si(2) and Y(1)′–O(5)–Si(2) are 111 and 142°. As a consequence of this bending, one phenyl ring of the bridging siloxide is located in the open region trans to O(5)′, with Y–C(ipso) = 3.02 Å and one Y–C(ortho) = 3.16 Å. It is noteworthy that the O–Si distance of the bridging siloxide is 5σ (0.032 Å) longer than for the terminal siloxides. This is consistent with other complexes containing both terminal and bridging siloxides.[1–4]



I

Solution Behavior. In view of the ease with which $Y_2(OSiPh_3)_6$ reacts with Lewis bases to form monomeric products, we sought to determine whether the solid-state structure of I persists in noncoordinating solvent. The ^1H and the ^{13}C NMR spectra in the phenyl region did not permit definitive structural assignment. The former is broad, and the latter contains a complex set of lines. Only a monomeric formulation can be excluded. We therefore recorded the ^{29}Si NMR spectrum of a quite dilute (yet saturated) solution in $CDCl_3$. Because this complex was so poorly soluble, an acquisition time in excess of 16 h was necessary to yield an acceptable spectrum. The spectrum shows two signals, with a 1:2 intensity ratio, at −17.1 and −26.1 ppm. The resonance for the bridging siloxide is broader than that for the terminal group, suggesting possible unresolved coupling to ^{89}Y (100% $I = {}^1/_2$). This indicates that the $X_2M(\mu\text{-}X)_2MX_2$ structure is retained in $CDCl_3$ and that bridge/terminal ligand exchange, if it occurs at all, is slow on the ^{29}Si NMR time scale. Thus, the distortion of the solid-state structure of $Y_2(OSiPh_3)_6$ does not foretell ready dissociation to monomeric $Y(OSiPh_3)_3$ in solution.

Discussion

Compounds related to the title compound are $Ce_2(OCH^tBu_2)_6$,[5]

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Table II. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $Y_2(OSiPh_3)_6$

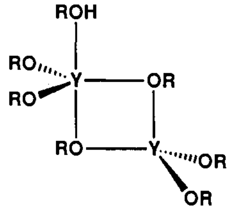
	x	*y*	*z*	$10B_{iso}$, Å^2
Y(1)	478 (1)	4582 (1)	9324.4 (3)	18
Si(2)	−683 (2)	3330 (2)	10480 (1)	20
Si(3)	−1174 (2)	4509 (2)	8040 (1)	24
Si(4)	2269 (2)	2949 (2)	9096 (1)	26
O(5)	−323 (3)	4186 (3)	10114 (2)	19
O(6)	−469 (4)	4544 (4)	8613 (2)	26
O(7)	1504 (4)	3640 (4)	9320 (2)	26
C(8)	−1280 (5)	2533 (5)	9975 (4)	23
C(9)	320 (5)	2792 (6)	10876 (3)	23
C(10)	−1521 (5)	3800 (5)	11030 (4)	23
C(11)	−2432 (5)	4439 (5)	8299 (4)	24
C(12)	−1027 (6)	5478 (6)	7545 (4)	29
C(13)	−924 (5)	3511 (6)	7588 (4)	26
C(14)	2505 (6)	3165 (5)	8287 (4)	26
C(15)	1815 (6)	1807 (6)	9173 (4)	32
C(16)	3366 (6)	3038 (6)	9561 (4)	28
C(17)	224 (6)	1976 (6)	11138 (4)	27
C(18)	941 (7)	1559 (7)	11425 (5)	43
C(19)	1821 (8)	1946 (8)	11458 (5)	49
C(20)	1954 (6)	2738 (7)	11208 (4)	41
C(21)	1212 (6)	3173 (6)	10927 (4)	31
C(22)	−1388 (6)	3692 (6)	11649 (4)	34
C(23)	−2043 (8)	4033 (7)	12042 (4)	47
C(24)	−2820 (7)	4480 (7)	11828 (5)	44
C(25)	−2948 (6)	4611 (6)	11226 (4)	35
C(26)	−2295 (7)	4273 (6)	10835 (4)	32
C(27)	−759 (7)	2059 (7)	9589 (5)	48
C(28)	−1148 (9)	1441 (7)	9209 (4)	51
C(29)	−2072 (8)	1308 (7)	9195 (5)	52
C(30)	−2617 (8)	1760 (9)	9577 (8)	93
C(31)	−2213 (7)	2366 (8)	9967 (7)	69
C(32)	−2589 (6)	4249 (7)	8896 (4)	37
C(33)	−3512 (7)	4150 (8)	9093 (5)	49
C(34)	−4238 (7)	4239 (7)	8705 (5)	43
C(35)	−4099 (6)	4419 (7)	8109 (5)	41
C(36)	−3190 (6)	4519 (6)	7915 (4)	33
C(37)	−185 (7)	5572 (7)	7240 (4)	41
C(38)	−47 (7)	6282 (7)	6870 (5)	47
C(39)	−702 (8)	6924 (7)	6815 (5)	50
C(40)	−1516 (7)	6851 (7)	7112 (5)	46
C(41)	−1684 (7)	6136 (6)	7467 (4)	37
C(42)	−818 (7)	3517 (6)	6971 (4)	35
C(43)	−652 (6)	2750 (8)	6662 (4)	41
C(44)	−537 (7)	1979 (7)	6957 (5)	46
C(45)	−639 (8)	1951 (7)	7567 (5)	50
C(46)	−816 (7)	2709 (6)	7878 (4)	41
C(47)	1795 (6)	3320 (7)	7875 (4)	37
C(48)	1914 (6)	3479 (7)	7280 (4)	42
C(49)	2833 (7)	3467 (7)	7070 (4)	38
C(50)	3572 (6)	3316 (7)	7460 (4)	36
C(51)	3429 (6)	3163 (6)	8059 (4)	28
C(52)	1556 (7)	1293 (6)	8688 (5)	42
C(53)	1193 (9)	461 (8)	8774 (6)	67
C(54)	1116 (11)	141 (7)	9350 (7)	76
C(55)	1364 (10)	642 (7)	9824 (6)	63
C(56)	1711 (7)	1465 (6)	9749 (5)	42
C(57)	4046 (7)	2374 (7)	9562 (4)	39
C(58)	4870 (7)	2448 (9)	9907 (5)	54
C(59)	5068 (7)	3146 (9)	10249 (4)	53
C(60)	4411 (7)	3800 (7)	10264 (5)	45
C(61)	3586 (7)	3752 (6)	9925 (4)	34
C(62)	4144 (13)	9936 (11)	9655 (8)	90 (4)
C(63)	4164 (12)	10155 (11)	10266 (8)	95 (5)
C(64)	5015 (13)	9789 (11)	9409 (7)	95 (4)
C(65)	3502 (27)	9785 (25)	9286 (17)	119 (9)

[a] Fractional coordinates are $\times 10^4$. [b] Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* **1959**, *12*, 609.

Table III. Selected Bond Distances (Å) and Angles (deg) for $Y_2(OSiPh_3)_6$

Y(1)–O(5)	2.211 (5)	Si(3)–C(11)	1.903 (8)
Y(1)–O(5)′	2.288 (5)	Si(3)–C(12)	1.872 (9)
Y(1)–O(6)	2.058 (5)	Si(3)–C(13)	1.879 (9)
Y(1)–O(7)	2.062 (5)	Si(4)–O(7)	1.613 (6)
Si(2)–O(5)	1.642 (5)	Si(4)–C(14)	1.875 (9)
Si(2)–C(8)	1.859 (8)	Si(4)–C(15)	1.884 (9)
Si(2)–C(9)	1.856 (8)	Si(4)–C(16)	1.860 (9)
Si(2)–C(10)	1.879 (8)	Y(1)–Y(1)′	3.581 (1)
Si(3)–O(6)	1.607 (6)		
O(5)–Y(1)–O(5)′	74.54 (20)	Y(1)–O(5)–Y(1)′	105.46 (20)
O(5)–Y(1)–O(6)	112.03 (20)	Y(1)–O(5)–Si(2)	111.06 (25)
O(5)′–Y(1)–O(6)	105.42 (20)	Y(1)–O(5)′–Si(2)′	142.5 (3)
O(5)–Y(1)–O(7)	131.76 (20)	Y(1)–O(6)–Si(3)	177.8 (3)
O(5)′–Y(1)–O(7)	101.01 (20)	Y(1)–O(7)–Si(4)	162.3 (4)
O(6)–Y(1)–O(7)	115.29 (22)		

$Y_2(OSiMe_2{}^tBu)_6({}^tBuMe_2SiOH)$,[1] and $Y_2(OAr)_6(THF)_2$ (Ar = 2,6-$Me_2C_6H_3$),[6] which all have two bridging groups. The (paramagnetic) cerium(III) compound is rigorously centrosymmetric and adopts the diborane structure. It shows no bridge/terminal exchange by ^1H NMR spectroscopy at 25 °C. The yttrium siloxide compound (II) is rapidly fluxional (500-MHz ^1H NMR) among all sites. The aryloxide dimer containing THF has the structure of two square based pyramids sharing a basal edge. Two distinct aryl environments are detected in the proton NMR spectrum of the ring methyls. The provisional conclusion from these and related[4] data is that exchange of μ_2 and terminal OR groups is not extremely facile *except* when it is proton-catalyzed (e.g., $Y_2(OSiMe_2{}^tBu)_6({}^tBuMe_2SiOH)$). This relates to intramolecular exchange, but it also implies that dissociation of Y_2 species into monometal fragments is not rapid on the NMR time scale. Taken together with the variable metal coordination number observed in Y_2 species, this suggests that the "bridge-splitting" reactions of eq 1–4 occur by an associative mechanism.



II (R = $^tBuMe_2Si$)

Acknowledgment. This work was supported by the Department of Energy.

Supplementary Material Available: Tables of full crystallographic details and anisotropic thermal parameters (3 pages); a listing of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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Gold(I) vs Gold(III): Stabilization of Two Gold(I) Polyselenide Complexes, $[Au_2(Se_2)(Se_3)]^{2-}$ and $[Au_2(Se_2)(Se_4)]^{2-}$, by the Diselenide Unit

Song-Ping Huang and Mercouri G. Kanatzidis*

Received December 26, 1990

Introduction

The synthesis, structural characterization, and reactivity of heavier metal polychalcogenide (i.e. polyselenide and polytelluride) compounds are currently an active area of research[1,2] after intense

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0020-1669/91/1330-3572$02.50/0