h) that the quantum yield of Co^{2+} is unaffected by the addition of ascorbic acid. Since the Ru(bpy)$_3^{3+}$–ascorbic acid reaction is almost diffusion controlled and the concentration of ascorbic acid is much higher than that of Co(en)$_3^{2+}$, the Co(en)$_3^{2+}$–Ru(bpy)$_3^{3+}$ reaction could not compete with the ascorbic acid–Ru(bpy)$_3^{3+}$ reaction. We could not measure the rate of the Co(NH$_3$)$_6^{2+}$–Ru(bpy)$_3^{3+}$ reaction.[14] However, although the rate for oxidation of Co(NH$_3$)$_6^{3+}$ by Ru(bpy)$_3^{3+}$ is probably[15] ~10 times faster than for oxidation of Co(en)$_3^{2+}$, the rate of ligand detachment for Co(NH$_3$)$_6^{2+}$ is also considerably faster ($k_{-L} > 7 \times 10^5$ s^{-1}). Undoubtedly, ligand loss from Co(NH$_3$)$_6^{2+}$ is considerably faster than oxidation by Ru(bpy)$_3^{3+}$, and mechanism 3 is also ruled out for Co(NH$_3$)$_6^{3+}$.

Mechanism 2 is ruled out by comparing the rate constants for cage separation ($k_d' \sim 1 \times 10^{10}$ s^{-1}, estimated from theoretical equations[16]) and for cage recombination ($k_{\mathrm{bel}} \sim 1 \times 10^7$ s^{-1} estimated from the measured value $k_f'k_{\mathrm{bel}}/k_d' = 5 \times 10^6$ M^{-1} s^{-1} and the calculated[16] value $k_f'/k_d' \sim 0.5$ M^{-1}). Evidently, cage recombination is much slower than cage separation and cannot account for the low yield of Co(II) for Co(en)$_3^{2+}$. Similarly, assuming that the rate of oxidation of Co(NH$_3$)$_6^{2+}$ is ~10 times faster than for Co(en)$_3^{2+}$,[15] cage recombination is too slow to compete with cage separation and mechanism 2 is ruled out for Co(NH$_3$)$_6^{3+}$ as well.

Our conclusion that mechanism 1, parallel energy- and electron-transfer pathways, is operative for quenching of *Ru(bpy)$_3^{2+}$ by Co(en)$_3^{3+}$ or Co(NH$_3$)$_6^{3+}$ receives additional support by recognizing that reactions of Co(NH$_3$)$_6^{3+}$, which proceed by electron transfer, are *invariably* faster than those of Co(en)$_3^{3+}$ (Table II).[15] The *observed* rate constants for quenching of *Ru(bpy)$_3^{2+}$ (and other (polypyridine)ruthenium(II) complexes) exhibit the opposite order, but when corrected for the energy-transfer contribution, the resulting *electron-transfer* quenching constants, 3.7 × 10^6 and 6.8 × 10^6 M^{-1} s^{-1} for Co(en)$_3^{3+}$ and Co(NH$_3$)$_6^{3+}$, respectively, conform to the normal reactivity pattern. The energy-transfer pathway demonstrated for Co(en)$_3^{3+}$ and Co(NH$_3$)$_6^{3+}$ quenching of *Ru(bpy)$_3^{2+}$ does not imply that the other Co(III) complexes studied by Sandrini et al.[8] also react by energy transfer. In fact, for Co(NH$_3$)$_5$Cl^{2+} (with $N_{\mathrm{Co}} = 1.05 \pm 0.06$, Table I) and in general for the more reactive complexes,[7] the predominant, if not exclusive, pathway for deactivation of *Ru(bpy)$_3^{2+}$ may well be electron transfer.

Finally we comment on the reported nonadiabatic factors of 0.1, 1 × 10^{-3}, and 1 × 10^{-5} for a variety of redox and quenching reactions of Co(NH$_3$)$_6^{3+}$ (and Co(NH$_3$)$_5$OH$_2^{3+}$), Co(en)$_3^{3+}$, and Co(phen)$_3^{3+}$ (and Co(bpy)$_3^{3+}$). Although the fits of the homogenized[17] rate constants to an empirical[18] dependence of $\Delta G^*(0)$ upon ΔG° are acceptable, we question the reliability of the derived values of κ and ΔG^* in the equation[17] $k = (k_d/k_{-d})(kT/h)\kappa \cdot \exp(-\Delta G^*/RT)$. First, combination of the fitted values[8] of κ and ΔG^* and the estimated[8] values of k_d and k_{-d} yields second-order rate constants of self-exchange for Co(NH$_3$)$_6^{3+/2+}$ (and Co(NH$_3$)$_5$OH$_2^{3+/2+}$), Co(en)$_3^{3+/2+}$, and Co(phen)$_3^{3+/2+}$ (and Co(bpy)$^{3+/2+}$) of 3.2 × 10^{-6}, 4.4 × 10^{-3}, and 3.8 × 10^{-2} M^{-1} s^{-1}, compared with experimental values of ~1 × 10^{-6}, 7.7 × 10^{-5}, and 4.2 × 10 M^{-1} s^{-1}. We regard any treatment of cross-reactions that is incompatible with the experimentally measured self-exchange rate constants and does not explain the discrepancy as suspect.[19] Second, the rate constants for quenching of *Ru(bpy)$_3^{2+}$ by Co(NH$_3$)$_6^{3+}$, Co(en)$_3^{3+}$, and Co(phen)$_3^{3+}$ [20] include contributions of energy transfer and, unless these contributions are subtracted, any treatment of the quenching constants as electron-transfer rate constants is flawed. Third, we note that the average ratio of $k_{\mathrm{Co(NH_3)_6^{3+}}}/k_{\mathrm{Co(en)_3^{3+}}}$ for the *redox* reactions listed in Table II (excluding[15] Ru(en)$_3^{2+}$) is 7 ± 5, in excellent agreement with the value of ~10 estimated from the adiabatic equation[21] $k_{12}/k_{13} = [k_{22}(\Delta E_{23}^\circ)/k_{33}]^{1/2}$. Moreover, the values of $k_{\mathrm{Co(en)_3^{3+}}}$ agree within a factor of less than 6 (excluding[15] Ru(en)$_3^{2+}$) with the calculated values utilizing Marcus' cross-reaction (ion-pair model), allowing for little nonadiabaticity in the reactions listed. In contrast, the reactions of the Co(II) complexes with Ru(bpy)$_3^{3+}$ appear to be nonadiabatic, as previously noted[7] for the corresponding reactions of Co(II) cage complexes.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE 8203887. A.H. is grateful to Drs. U. Fürholz and N. Sutin for several illuminating discussions.

Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; Co(NH$_3$)$_6^{3+}$, 14695-95-5; Co(en)$_3^{3+}$, 14878-41-2; Co(NH$_3$)$_5$Cl^{2+}, 14970-14-0.

Department of Chemistry
State University of New York
Stony Brook, New York 11794

Khurram Zahir
Wolfhardt Böttcher
Albert Haim*

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Organosilicates as Silica Surface Models: The Molybdenum Trioxide Complexes R$_3$SiOMoO$_3^-$, Where R = Phenyl and *tert*-Butyl

Sir:

Molybdenum trioxide supported on silica can serve as a catalyst or a catalyst precursor for a variety of reactions,[1] including the partial oxidation of alkanes,[2,3] alkenes,[4] and alcohols;[5] olefin metathesis;[6] and thiophene hydrodesulfurization.[7] Despite numerous attempts to characterize MoO$_3$/SiO$_2$,[8] the active chemical species remain obscure due to the insoluble and amorphous nature of the material and the absence of well-characterized compounds that model its spectroscopic and chemical properties. As part of a more general program concerned with modeling oxide surface hydroxyl groups, we have begun to investigate the synthesis, characterization, and reactivity of organosilicate–molybdate complexes. The simplest conceivable complexes of this type, R$_3$SiOMoO$_3^-$ (R = C$_6$H$_5$, *t*-C$_4$H$_9$), are reported here as crystalline (n-C$_4$H$_9$)$_4$N$^+$ salts that are soluble and indefinitely stable in aprotic media.

Following the classical method of preparing MoO$_3$/SiO$_2$ from SiO$_2$ and aqueous (Mo$_7$O$_{24}$)(NH$_4$)$_6$,[9] we have treated 0.05 M

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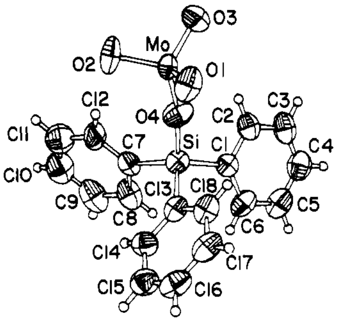


Figure 1. ORTEP drawing of the $(C_5H_5)_3SiOMoO_3^-$ anion in crystalline **1**. The molybdenum, silicon, oxygen, and carbon atoms are represented by thermal vibration ellipsoids drawn to encompass 35% of the electron density. Hydrogen atoms are represented by arbitrarily sized spheres. Selected bond lengths and angles: Mo–O1 = 1.696 (4), Mo–O2 = 1.690 (4), Mo–O3 = 1.711 (4), Mo–O4 = 1.884 (4), O4–Si = 1.616 (4), Si–C(av) = 1.861 Å; Mo–O4–Si = 160.7 (3)°. The O–Mo–O angles vary between 108.9 (2) and 110.4 (2)°.

solutions of R_3SiOH (R = C_6H_5,[10] t-C_4H_9[11]) in CH_3CN with stoichiometric $(Mo_2O_7)[(n\text{-}C_4H_9)_4N]_2$[12] at 30 °C for 1 h according to eq 1 to yield $(R_3SiOMoO_3)[(n\text{-}C_4H_9)_4N]$, where R = C_6H_5

$$R_3SiOH + {}^1/{}_2Mo_2O_7{}^{2-} = R_3SiOMoO_3{}^- + {}^1/{}_2H_2O \quad (1)$$

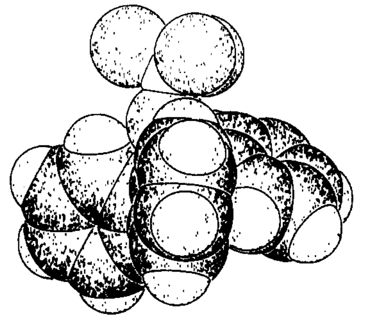
(**1**) and t-C_4H_9 (**2**). Colorless prismatic crystals of both compounds are obtained in >70% yield by addition of diethyl ether to the reaction solutions and cooling to −20 °C.[13]

The $R_3SiOMoO_3^-$ anion structure in **1** was established by a single-crystal X-ray diffraction study[14] (see Figure 1). Compound **2** is presumed to contain an isostructural anion according to solution and solid-state IR spectroscopic data.[13,16] Comparison of Mo–O bond lengths and angles in **1** with those in $(Mo_2O_7)[(n\text{-}C_4H_9)_4N]_2$[12] and Si–O/Si–C bond lengths with those in $[(C_6H_5)_3Si]_2O$[17] show very similar geometries at Mo and Si, respectively. The role played by the bulky $(C_6H_5)_3SiO^-$ supporting ligand is clearly illustrated in a space-filling representation, A.

Table I. IR Spectroscopic Data for $XMoO_3^-$ Anions

anion	str freq, cm^{-1}			
	ν_{Si-OMo}	ν_{MoO_3} (A_1)	ν_{MoO_3} (E)	ν_{Mo-OSi}
$(t\text{-}C_4H_9)_3SiOMo_3^{-\,a}$	974	901	878	333
$(C_6H_5)_3SiOMoO_3^{-\,a}$	983	906	884	329
$ClMoO_3^{-\,b}$		934	894	

[a] Present study: see ref 16 for details. [b] Data from: Königer-Ahlborn, E.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 574.



A

The larger $(t\text{-}C_4H_9)_3SiO^-$ ligand, like its $(t\text{-}C_4H_9)_3CO^-$ congener,[18] is even more effective in isolating the MoO_3 unit from its environment.

Compounds **1** and **2** show intense, sharp IR absorptions assigned to silicon–oxygen and molybdenum–oxygen stretching vibrations (see Table I).[13,16] Comparison of the MoO_3 stretching frequencies with those for $ClMoO_3^-$, also given in Table I, show the expected shifts due to changes in ligand donor properties. The observation and assignment of all the Si–O and Mo–O stretching vibrations in **1** and **2** should help to resolve the often-conflicting assignments of vibrational bands observed for MoO_3/SiO_2.[8c] This information plus the availability of newly developed thin-silica-film IR techniques[19] may allow better structural characterization of solid oxide supported molybdenum trioxide.

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(13) (a) Compound **1**: Anal. Calcd for $C_{34}H_{51}NSiMoO_4$: C, 61.71; H, 7.77; N, 2.12; Mo, 14.50. Found: C, 61.48; H, 7.61; N, 2.16; Mo, 14.77. ^1H NMR (CH_3CN-d_3, 20 °C): δ 7.4–7.6 ($(C_6H_5)_3Si$, m). $^{13}C\{^1H\}$ NMR (CH_3CN-d_3, 20 °C): δ 137.8, 135.6, 130.7, 128.7 ($(C_6H_5)_3Si$, s). $^{29}Si\{^1H\}$ NMR (CH_3CN, 20 °C, 0.015 M $Cr(acac)_3$): δ −17.6 (s). IR (Nujol mull, 1200–250 cm^{-1}, ±2 cm^{-1}): 1156 (w), 1113 (m), 1106 (sh), 1031 (m), 1003 (m), 983 (s), 906 (s), 884 (s), 858 (sh), 748 (m), 737 (m), 707 (s), 554 (w), 513 (s), 451 (w), 428 (w), 329 (m). The strong IR absorptions observed in Nujol mulls between 1200 and 550 cm^{-1} were observed at the same frequencies (±5 cm^{-1}) in CH_3CN solution. (b) Compound **2**: Anal. Calcd for $C_{28}H_{63}NSiMoO_4$: C, 55.88; H, 10.55; N, 2.33; Mo, 15.94. Found: C, 55.66; H, 10.50; N, 2.33; Mo, 15.66. ^1H NMR (CH_3CN-d_3, 20 °C): δ 1.09 ($(CH_3)_3CSi$, s). $^{13}C\{^1H\}$ NMR (CH_3CN-d_3, 20 °C): δ 30.3 ($(\mathit{C}H_3)_3CSi$, s), 24.5 ($(CH_3)_3\mathit{C}Si$, s). $^{29}Si\{^1H\}$ NMR (CH_3CN, 20 °C, 0.015 M $Cr(acac)_3$): δ 7.2 (s). IR (Nujol mull, 1200–250 cm^{-1}, ±2 cm^{-1}): 1172 (w), 1155 (w), 1107 (w), 1063 (w), 1014 (m), 1007 (m), 974 (s), 928 (m), 901 (s), 878 (s), 818 (s), 738 (m), 723 (m), 623 (s), 469 (m), 413 (w), 385 (w), 333 (m). The strong absorptions observed in Nujol mulls between 1200 and 550 cm^{-1} were observed at the same frequencies (±4 cm^{-1}) in CH_3CN solution.

(14) Colorless single crystals of $[(C_6H_5)_3SiOMoO_3][(n\text{-}C_4H_9)_4N]$ are monoclinic, space group $P2_1/n$, with a = 9.466 (2) Å, b = 23.114 (6) Å, c = 16.609 (3) Å, β = 100.05 (2)°, V = 3578 (1) Å^3, Z = 4, d_{calcd} = 1.228 g/cm^3, μ_{calcd} = 4.22 cm^{-1}. X-ray diffraction data at 25 °C were collected on a 0.2 × 0.3 × 0.5 mm crystal for 8267 independent reflections having $2\theta < 55°$ and for $\pm h,\pm k,\pm l$, on a Syntex P2$_1$ automated four-circle diffractometer using graphite-crystal monochromated Mo Kα radiation, λ = 0.71069 Å, and θ–2θ scans. The space group was unambiguously determined from systematic absences: $0k0$, $k = 2n$; $h0l$, $h + l = 2n$. The nonunique data were averaged, and the data were corrected for Lorentz, polarization, anomalous dispersion, crystal decay (<4%) and absorption effects; for the last, the maximum and minimum transmission factors were 0.924 and 0.882. The structure was solved by direct methods (MULTAN[15]). The final residuals for 371 variables refined against the 3112 data for which $I > 2.58\sigma(I)$ were R_F = 4.6%, R_w = 4.8%. In the final cycle, hydrogen atom positions were predicted and included in the structure factor calculations and an isotropic thermal parameter was refined for the group.

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the X-ray crystal structure determination. We are grateful to Dr. Egbert Keller for providing a copy of his SCHAKAL program.

Registry No. 1, 96212-33-8; **2**, 96212-35-0; $(Mo_2O_7)[(n\text{-}C_4H_9)_4N]_2$, 96211-57-3; MoO_3, 1313-27-5; SiO_2, 7631-86-9.

Supplementary Material Available: Table II (atomic coordinates for non-hydrogen atoms in **1**), Table III (atomic coordinates for hydrogen atoms in **1**), Table IV (thermal parameters for atoms in **1**), Figure 2 (ORTEP drawing of the cation in **1**), and structure factor tables for the X-ray structural study of **1** (17 pages). Ordering information is given on any current masthead page.

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[20] This author performed work for this paper while at both institutions. Present address: University of Illinois.

Department of Chemistry
University of Illinois
Urbana, Illinois 61801

W. G. Klemperer*[20]
V. V. Mainz
R.-C. Wang

Department of Chemistry
Columbia University
New York, New York 10027

W. Shum

Received January 23, 1985

A New Structural Form of Tin Octahedrally Coordinated in a Drum-Shaped Molecule[1]

Sir:

Although oligomeric organotin oxycarboxylates based on the composition $[RSn(O)O_2CR']_n$ have been known for some time,[2] no indications of their possible structural features are available. As early as 1921 some members of this class were reported[3] to be hexameric, e.g., $[CH_3Sn(O)O_2CR]_6$.

We report herein the synthesis and X-ray crystal structure of hexameric phenyltin oxycyclohexanecarboxylate, $[PhSn(O)O_2CC_6H_{11}]_6$. The X-ray characterization shows tin(IV) present in a new structural environment appearing as a drum-shaped molecule containing hexacoordinated tin atoms.

During the course of our work[4,5] on triorganotin esters of carboxylic acids, we first obtained the hexamer while recrystallizing triphenyltin cyclohexanoate, $Ph_3SnO_2C(C_6H_{11})$. Presumably, it formed as a result of slow hydrolysis of the latter compound with the loss of two molecules of benzene. A more direct route involves the reaction of $PhSnCl_3$ with the sodium salt of the acid in CCl_4 solution, followed by a hydrolysis step which gave the compound as a powdery substance in modest yield[6] present in a mixture of products:

$$\begin{array}{l} PhSnCl_3 + Na^+C_6H_{11}CO_2^- \xrightarrow{CCl_4} PhSn(Cl_2)O_2CC_6H_{11} + NaCl \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \downarrow{+H_2O} \\ \qquad\qquad\qquad\qquad\qquad\qquad PhSn(O)O_2CC_6H_{11} + 2HCl \end{array}$$

Although a pure product has yet to be obtained by this route, both the crystalline hexamer and the powder had similar Nujol mull infrared spectra, melted with decomposition at 340 °C, and were insoluble in organic solvents and in water. It thus appears that the hexamer is hydrolytically and thermally stable.

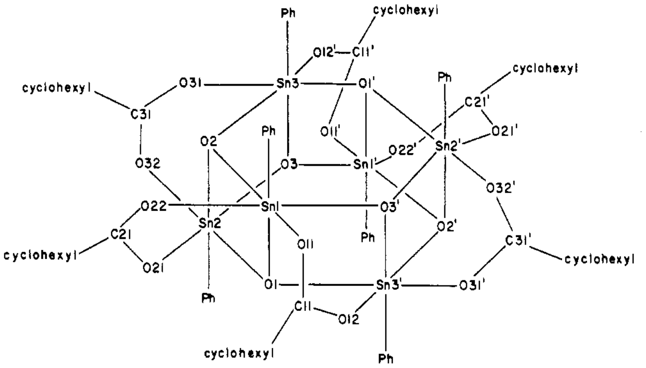

Figure 1. Schematic representation of the drum structure of $[PhSn(O)O_2CC_6H_{11}]_6$.

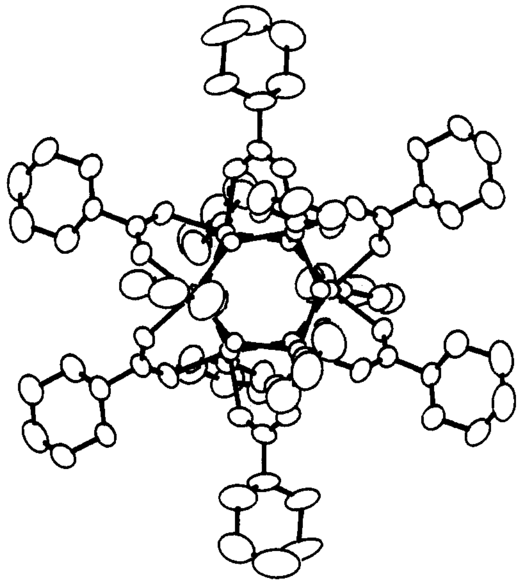

Figure 2. ORTEP plot of $[PhSn(O)O_2CC_6H_{11}]_6$ viewed down the S_6 axis with thermal ellipsoids at the 50% probability level.

The schematic in Figure 1 portrays the drum-shaped structure resulting from the X-ray analysis[7] and shows the atom labeling. The high symmetry associated with the molecule is revealed in Figure 2. The hexamer has crystallographic C_i symmetry. However, the noncrystallographic symmetry of the molecule is higher, namely S_6, assuming free rotation about the C–C single bonds.

The six tin atoms are chemically equivalent, as are the six trivalent oxygen atoms. The Sn–O framework of the molecule can be described as a drum with top and bottom faces each being comprised of a six-membered $(\text{–Sn–O–})_3$ tristannoxane ring.

The drum faces are joined together by six Sn–O bonds containing tricoordinated oxygen atoms. The sides of the drum are thus comprised of six four-membered $(\text{–Sn–O–})_2$ distannoxane rings, each of which is spanned by a carboxylate group that forms a symmetrical bridge between two tin atoms. The sides of the structure are reminiscent of the ladder arrangement in dimeric

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(6) Phenyltin trichloride (1.1 g, 3.6 mmol) and the sodium salt of cyclohexanecarboxylic acid (0.55 g, 3.6 mmol) were reacted in carbon tetrachloride (100 mL) at reflux temperature for 2 h. Filtration of NaCl and removal of the solvent in vacuo yielded a residue that was heated with a mixture of 95% ethanol (10 mL), acetonitrile (10 mL), and water (5 mL) for 2 h. A white insoluble compound was isolated (0.3 g); 25% yield, mp 340 °C dec. The infrared spectrum of this compound in Nujol shows $\nu(CO_2)$ at 1530 cm^{-1}.

(7) The hexameric stannoxane $[PhSn(O)O_2CC_6H_{11}]_6$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.919$ (3) Å, $b = 19.361$ (3) Å, $c = 15.089$ (2) Å; $\beta = 90.81$ (1)°, $Z = 2$, $\mu_{MoK\bar{\alpha}} = 1.891$ mm^{-1}. A total of 5984 independent reflections were measured at room temperature with use of the θ–2θ scan mode and graphite-monochromated Mo$K\bar{\alpha}$ radiation, for $2° \leq 2\theta_{MoK\bar{\alpha}} \leq 47°$, on an Enraf-Nonius CAD4 diffractometer. No corrections were made for absorption. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, hydrogen atoms fixed isotropic, function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{1/2} = 2F_oLp/\sigma_I$) led to $R = 0.030$ and $R_w = 0.044$ for the 5093 reflections having $I \geq 2\sigma_I$.

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