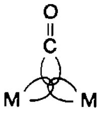
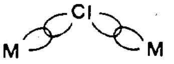
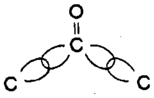


I

II



III



IV

does cause large differences in the M–M distance.[14-16] This fact underscores the similarities between the three-center bonding patterns of the M–C(O)–M and M–H–M[17] linkages (I and II), as opposed to the M–X–M bridging halide system, which represents a system with two localized σ bonds (III). The fluxionality of the M–C(O)–M[18] and M–H–M[19] systems, in contrast to the relative rigidity of the M–X–M and organic carbonyl (IV) systems, is also consistent with this idea.

Finally, we note that the coordination about Fe is not strictly octahedral. In $[HFe_2(CO)_8]^-$ the terminal carbonyl groups are not collinear with the bridging atoms, as evidenced by the C(t)–Fe–C(b) and C(t)–Fe–H angles of 164 (1) and 164 (3)°, respectively. The bridging CO and H groups are situated closer to the Fe–Fe bond than they would be if the above angles were 180°. This, again, is consistent with the general pattern of ligands found in $Fe_2(CO)_9$ [C(t)–Fe–C(b) = 172.1 (1)°].[10]

While $Co_2(CO)_8$ is known to exist in solution in both the carbonyl-bridged and nonbridged forms,[20] there is no evidence that either $[FeCo(CO)_8]^-$[21,2c] or $[HFe_2(CO)_8]^-$ exists in a similar equilibrium. The Nujol mull spectrum of $[(Ph_3P)_2N]^+[HFe_2(CO)_8]^-$ [1990 (m), 1920 (s), 1880 (vs), 1790 (m), 1750 (m), cm^{-1}] somewhat resembles the compound's THF solution spectrum[5b] [1987 (s), 1940 (s), 1880 (s), 1802 (s), 1770 (m) cm^{-1}]: the peaks of the solid-state spectrum are shifted to higher energies by varying amounts (between 0 and 20 cm^{-1}) in solution. Collman and co-workers have further shown that the Li^+ and Na^+ salts of $[HFe_2(CO)_8]^-$ in THF solution contain an additional band (1680 cm^{-1} for the Li^+ salt and 1730 cm^{-1} for the Na^+ salt) that can be attributed to ion-pairing effects. At any rate, all spectra clearly show the presence of bridging carbonyls, and, thus, it is likely that the structure described in this paper persists in solution.

Acknowledgment. We thank the National Science Foundation (Grants CHE-74-01541 and CHE-77-00360) for financial support of this research.

Registry No. $[(Ph_3P)_2N]^+[HFe_2(CO)_8]^-$, 66016-59-9.

Supplementary Material Available: A listing of the observed and calculated structure factors for $[(Ph_3P)_2N]^+[HFe(CO)_8]^-$ (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. Bau, R. G. Teller, S. W. Kirtley, and T. F. Koetzle, *Acc. Chem. Res.*, in press.

(2) (a) M. B. Smith and R. Bau, *J. Am. Chem. Soc.*, **95**, 2388 (1973); (b) R. Bau, S. W. Kirtley, T. N. Sorrell, and S. Winarko, *ibid.*, **96**, 988 (1974); (c) H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *ibid.*, **96**, 5285 (1974); (d) R. D. Wilson and R. Bau, *ibid.*, **96**, 7601 (1974); (e) R. D. Wilson, S. A. Graham, and R. Bau, *J. Organomet. Chem.*, **91**, C49 (1975); (f) H. B. Chin and R. Bau, *J. Am. Chem. Soc.*, **98**, 2434 (1976); (g) R. G. Teller, R. G. Finke, J. P. Collman, H. B. Chin, and R. Bau, *ibid.*, **99**, 1104 (1977).

(3) W. Hieber and G. Brendel, *Z. Anorg. Allg. Chem.*, **289**, 324 (1957).

(4) (a) K. Farmery, M. Kilner, R. Greatrex, and N. N. Greenwood, *Chem. Commun.*, 593 (1968); (b) *J. Chem. Soc. A*, 2339 (1969).

(5) (a) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 4685 (1976); (b) J. P. Collman, R. G. Finke, P. L. Matlock, R. Wahren, R. G. Komoto, and J. I. Brauman, *ibid.*, **100**, 1119 (1978).

(6) J. K. Ruff and W. J. Schlientz, *Inorg. Synth*, **15**, 84 (1974).

(7) The positions of the phenyl hydrogen atoms were calculated by assuming an idealized sp^2 hybridization of the carbon atoms and a C–H bond distance of 1.1 Å.

(8) (a) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973); (b) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

(9) (a) $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = \{\sum w||F_o| - |F_c||^2/\sum wF_o^2\}^{1/2}$. (b) The major computations in this work were performed using CRYM, an amalgamated set of crystallographic programs developed by Dr. R. E. Marsh and co-workers at the California Institute of Technology.

(10) F. A. Cotton and J. M. Troup, *J. Chem. Soc., Dalton Trans.*, 800 (1974).

(11) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).

(12) (a) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965); (b) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 1351 (1969).

(13) P. S. Braterman, *Struct. Bonding (Berlin)*, **10**, 57 (1972).

(14) One can, for example, make the following sets of comparisons: Mo–Mo = 2.665 Å in $[Cl_3Mo(\mu\text{-}Cl)_3MoCl_3]^{3-}$ and 2.380 Å in $[Cl_3Mo(\mu\text{-}Cl)_2(\mu\text{-}H)MoCl_3]^{3-}$; Mo–Mo = 2.816 Å in $[Br_3Mo(\mu\text{-}Br)_3MoBr_3]^{3-}$ and 2.439 Å in $[Br_3Mo(\mu\text{-}Br)_2(\mu\text{-}H)MoBr_3]^{3-}$;[15] Rh–Rh = 3.719 Å in $[(C_5Me_5)RhCl]_2(\mu\text{-}Cl)_2$ and 2.906 Å in $[(C_5Me_5)RhCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$;[16] Ir–Ir = 3.769 Å in $[(C_5Me_5)IrCl]_2(\mu\text{-}Cl)_2$ and 2.903 Å in $[(C_5Me_5)IrCl]_2(\mu\text{-}H)(\mu\text{-}Cl)$.[16]

(15) F. A. Cotton and B. J. Kalbacher, *Inorg. Chem.*, **15**, 522 (1976).

(16) M. R. Churchill and S. A. Julis, *Inorg. Chem.*, **16**, 1488 (1977).

(17) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. A. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974).

(18) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *Inorg. Chem.*, **14**, 511 (1975), and references therein.

(19) R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, **99**, 3872 (1977).

(20) (a) K. Noack, *Spectrochim. Acta*, **19**, 1925 (1963); (b) G. Bor, *ibid.*, **19**, 2065 (1963).

(21) J. K. Ruff, *Inorg. Chem.*, **7**, 1818 (1968).

Contribution from Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University California, Berkeley, California 94720

Structure of Tris(bis(trimethylsilyl)amido)neodymium(III), $Nd[N(Si(CH_3)_3)_2]_3$[1]

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Neodymium tris(bis(trimethylsilyl)amide) is the only known monomeric, three-coordinate derivative of this lanthanide element.[2] The structures of the europium(III)[3] and ytterbium(III)[4] derivatives have been examined by X-ray crystallographic techniques and they, along with the scandium(III) analogue,[3] have been shown to have MN_3 skeletons which are not planar. In contrast all other crystallographically known tris(silylamides) of the type $M[N(SiMe_3)_2]_3$ are planar.[4] We describe the crystal structure of $Nd[N(SiMe_3)_2]_3$ and show that it is also nonplanar.

Experimental Section

The $Nd[N(SiMe_3)_2]_3$ was prepared as previously described,[2] mp 157–161 °C (lit.[2] 161–164 °C). The crystal used in the X-ray analysis was taken from a batch crystallized from pentane (0 °C).

Magnetic susceptibility measurements were obtained with a PAR Model 155 vibrating sample magnetometer employing a homogeneous magnetic field produced by a Varian Associates 12-in. electromagnet capable of a maximum field strength of 12.5 kG. The magnetometer was calibrated with $HgCo(CNS)_4$.[5] A variable-temperature liquid-helium system produced sample temperatures in the range 4–100 K. The temperature was measured with a calibrated GaAs diode.

A hexagonal needle-shaped crystal, 0.09 mm across and 0.3 mm long, was sealed inside a quartz capillary in an argon-filled drybox. It was examined with a Picker FACS-I automatic diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1)$ 0.7093 Å). ω scans of several low-angle reflections showed peaks with half-widths of 0.16 and 0.21° for $h00$ and $00l$ type reflections, respectively. The space group was identified as $P\bar{3}1c$. The setting angles of 12 manually centered reflections ($19 < 2\theta < 25°$) were used to determine by least-squares the cell parameters $a = 16.476$ (13) Å, $c = 8.485$ (7) Å, and $V = 1995$ Å^3. For $Z = 2$ and a molecular

Table I. Positional and Thermal Parameters[a] with Estimated Deviations[b] for $Nd[N(Si(CH_3)_3)_2]_3$

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Nd[c]	2/3	1/3	0.2903 (3)	3.49 (7)					
N[c]	0.508 (1)	0.254	1/4	4.3 (7)	4.7 (6)	2.4 (7)	2.15	0	0.3 (5)
Si	0.4543 (3)	0.2866 (3)	0.1131 (5)	4.5 (2)	5.4 (2)	4.0 (2)	2.8 (2)	−0.6 (2)	−0.1 (2)
C(1)	0.401 (1)	0.353 (1)	0.202 (2)	8 (1)	9 (1)	8 (1)	6 (1)	1 (1)	−1 (1)
C(2)	0.364 (1)	0.187 (1)	−0.005 (2)	6 (1)	8 (1)	7 (1)	2 (1)	−4 (1)	−1 (1)
C(3)	0.546 (1)	0.367 (1)	−0.033 (2)	7 (1)	8 (1)	4 (1)	4 (1)	1 (1)	3 (1)

[a] The anisotropic temperature factor has the form $\exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots))$. [b] Here and in the following tables the numbers in parentheses are the estimated standard deviations in the least significant digit. [c] Symmetry conditions of the special positions for N; $x = 2y$, $B_{11} = 2B_{12}$, and $B_{13} = 0$.

Table II. Interatomic Distances (Å)

bond	distance	corrected[a]
Nd-3N	2.29 (2)	2.29
N-2Si	1.70 (1)	1.71
Si-C(1)	1.88 (2)	1.91
Si-C(2)	1.86 (2)	1.90
Si-C(3)	1.89 (2)	1.91

[a] Adjusted for thermal motion assuming the "riding" model.

Table III. Selected Angles (deg)

N-Nd-N	117.8 (1)	N-Si-C(2)	114.0 (7)
Nd-N-Si	123.2 (5)	N-Si-C(3)	108.0 (7)
Nd-N-Si[a]	110.1 (4)	C(1)-Si-C(2)	108.9 (9)
Si-N-Si[a]	126.4 (9)	C(1)-Si-C(3)	107.2 (8)
N-Si-C(1)	112.4 (6)	C(2)-Si-C(3)	105.9 (8)

[a] Atom at position x, $x - y$, $^1/_2 - z$.

weight of 625.4 the calculated density is 1.04 g cm^{-3}.

Intensity data were collected using the θ–2θ scan technique with a scan speed of 2°/min on 2θ. Each peak was scanned from 0.75° before the $K\alpha_1$ peak to 0.75° after the $K\alpha_2$ peak, and backgrounds were counted for 10 s at each end of the scan range, offset by 0.5°. The needle direction of the crystal was approximately parallel to the φ axis of the diffractometer. The temperature during data collection was 21 ± 1 °C. Three standard reflections (300, 060, and 002) were measured after every 200th scan; no significant variation was observed in the intensities of the first two reflections, and a 5% decay in intensity was observed for the 002 reflection. A linear decay correction of about 4% was applied uniformly to the data. The absorption coefficient is estimated to be 15 cm^{-1}. Because of the diffraction geometry and the small crystal dimensions, the absorption is small and no correction was deemed necessary. A total of 3404 scans, not including standards, resulted in 917 unique reflections, 535 of which were greater than 2σ.

The positions of the Nd, N, and Si atoms were deduced from a three-dimensional Patterson function. The carbon atoms were obtained from a subsequent least-squares and Fourier calculation. A series of least-squares refinements in which the function $\sum w(|F_o| - |F_c|)^2/\sum wF_o^2$ was minimized converged to the final structure. The expressions that were used in processing the data and estimating the weights are given in the supplementary material; the "ignorance factor", p, was set to 0.06. Scattering factors from Doyle and Turner[6] were used, and dispersion corrections[7] were applied. Hydrogen atoms could not be located and were not included. Because of the large residuals exhibited by several of the low-angle intensities, all 35 data whose $(\sin\theta)/\lambda$ is less than 0.127 were deleted. The discrepancy indexes for 522 data are

$$R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.076$$

$$R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.091$$

R for all 882 data is 0.13. The error in an observation of unit weight is 2.0. In the last cycle no parameter changed more than 0.001σ.

Results and Discussion

Atomic parameters, distances, and angles are listed in Tables I–III. The molecular structure of this Nd complex (Figure 1) is similar to that found in the Al,[8] Fe,[9] Sc,[3] and Eu[3] compounds. The Nd atom is on a crystallograhic threefold axis and is bonded to three nitrogen atoms. In the Sc and Eu isomorphs[4] the metal atoms are disordered in the z direction and were treated as two half atoms ~0.6 Å above and below the plane at $z = ^1/_4$. This structure is similar with Nd 0.34 Å above and below $z = ^1/_4$. Originally the Nd atom was treated as an anisotropic atom at $z = ^1/_4$ which resulted in thermal parameters B_{11} and B_{33} being 3.5 and 16.0 Å^2, respectively. When the Nd atom was treated isotropically as two half atoms disordered across the plane at $z = ^1/_4$ the subsequent least-squares refinement resulted in the R factor going from 0.084 for the ordered to 0.076 for the disordered description.

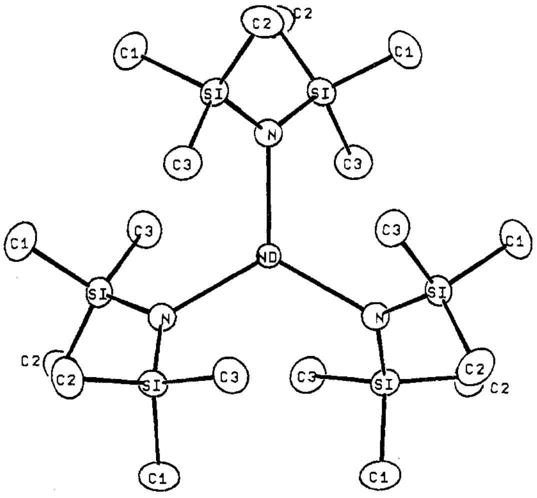

Figure 1. ORTEP view of $Nd[N(SiMe_3)_2]_3$ down the c axis.

A large channel that runs up the z axis, at the origin of the unit cell, is characteristic of the structures of these hexagonal $M[N(SiMe_3)_2]_3$ complexes. Hursthouse and Rodesiler[9] have shown that in the case of the iron complex the channel is large enough to accommodate a benzene ring with the plane of the ring perpendicular to the z axis; they could not find any ordered solvent in the channel. A search of the final electron density and difference maps for the Nd structure showed one peak at 0, 0, $^1/_4$ of about 3 e/Å^3 and three peaks between 0.4 and 1.0 e/Å^3 just off the axis. The pattern of these peaks did not resemble any reasonable molecule that might have been used in the synthesis. It must be presumed that the channel, if occupied, contains solvent molecules that are so irregularly located as to be virtually invisible to the X-ray diffraction technique. The large R factor and the large error of a reflection of unit weight may be a result of this unresolved structure.

The variable-temperature (4.2–89.6 K) magnetic susceptibility follows Curie–Weiss behavior, $\chi = C_M/(T + \Theta)$, $C_M = 1.33$ and $\Theta = 12$ K. The magnetic moment, μ_{eff}, is 3.27 μ_B.

Acknowledgment. We thank Dr. N. M. Edelstein for useful discussions.

Supplementary Material Available: Data processing formulas and the listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work was supported by the Division of Basic Energy Sciences of the Department of Energy.
(2) D. C. Bradley, J. S. Ghotra, and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1021 (1973).
(3) J. S. Ghotra, M. B. Hursthouse, and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 669 (1973).
(4) P. G. Eller, D. C. Bradley, M. B. Hursthouse, and D. W. Meek, *Coord. Chem. Rev.*, **24**, 1 (1977).
(5) H. St. Räde, *J. Phys. Chem.*, 77, 424 (1973).
(6) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
(7) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(8) G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. A*, 2279 (1969).
(9) M. B. Hursthouse and P. F. Rodesiler, *J. Chem. Soc., Dalton Trans.*, 2100 (1972).

Contribution from the Inorganic Chemistry Laboratory, Oxford University, Oxford, England, and the CNRS Laboratoire de Magnetisme and Institut Laue-Langevin, Grenoble, France

Neutron Diffraction of Mixed-Valence $CsAuCl_3$ at High Pressure

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Wells's salt,[1] whose empirical formula is $CsAuCl_3$, is a classical example of a class II[2] mixed-valence compound. Its crystal structure, first determined by Elliot and Pauling[3] in 1938, and recently refined,[4] reveals that half the gold atoms are surrounded by four chlorine atoms in a plane while the other half have two chlorine nearest neighbors in a linear arrangement. Since square-planar coordination is typical of the low-spin d^8 configuration and linear coordination of d^{10}, it is clear that to a first approximation the lattice contains Au(I) and Au(III), and not Au(II). This agrees with the facts that it is diamagnetic and at ambient pressure is a high-resistance semiconductor. Nevertheless, in contrast to the $AuCl_4^-$ and $AuCl_2^-$ ions, which are both pale yellow, it is black. Thus, the Franck–Condon barrier to intervalence electron transfer cannot be greater than about 2 eV, and, in fact, in a closely related ammonium salt an absorption edge was found at 2.2 eV.[5]

Recently, however, it has been reported[6] that the electrical conductivity of $CsAuCl_3$ is a very steep function of hydrostatic pressure, increasing continuously by 9 orders of magnitude up to 60 kbar, when it behaves as a metal. Clearly, such a transformation must be accompanied by some alteration in the structure. At first sight $CsAuCl_3$ appears to contain chains of alternate $AuCl_4^-$ and $AuCl_2^-$, the planes of the former perpendicular to the *c* axis and the axes of the latter along this axis. However, as pointed out by Wells[7] the three-dimensional structure of $CsAuCl_3$ can be considered formally as derived from the cubic perovskite structure by displacing the chloride ions from the centers of the cube edges in the fashion shown in Figure 1. Thus, a reasonable hypothesis would be that the transformation of $CsAuCl_3$ from a high-resistance semiconductor at ambient pressure to a metal at 60 kbar is brought about by the movement of the chloride ions toward the centers of the lines joining every nearest-neighbor pair of gold atoms. Every gold atom would have an identical environment and the Franck–Condon barrier to electron transfer between the metal sites would disappear; i.e., the compound would become a class III[2] mixed-valence material. In an attempt to verify this hypothesis we have performed powder neutron diffraction measurements on $CsAuCl_3$ under pressure. This note reports our results.

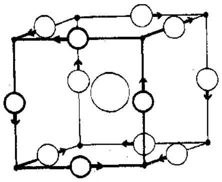

Figure 1. Relation between the structure of $CsAuCl_3$ and the cubic perovskite structure. Small filled circles are Au, smaller open circles are Cl, and the large open circle is Cs.

Table I. Neutron Diffraction and Unit Cell Parameters of $CsAuCl_3$ at Various Pressures

	P, kbar	2θ(obsd)	2θ(calcd)	a_0	c_0
(110)	0	13.15 ± 0.05		7.53	
	1	13.18		7.52	
	20	13.42		7.38	
	28	13.50		7.34	
(202,022)	0	22.90	22.75		
	1	22.95	22.80		
	20	23.35	23.23		
	28	23.40	23.38		
(004)	0	26.03			10.84
	1	26.05			10.83
	20	26.60			10.61
	28	26.80			10.53

Experimental Section

$CsAuCl_3$ was prepared according to Wells.[1] The powder neutron diffraction data were collected at room temperature on the D2 diffractometer at the Institut Laue-Langevin, Grenoble, using a wavelength of 1.222 Å. The sample was contained in an aluminum can within a portable and compact high-pressure clamped cell[7] made of Lucalox (high-density alumina). A small quantity of NaCl was placed inside the sample can as an internal pressure calibrant. Scans were also run on the sample within its can but without the pressure cell.

Results and Discussion

An inevitable consequence of the experimental setup is the presence of a large number of intense reflections from the Al_2O_3, Al, and NaCl which obscure about two-thirds of the reflections from the sample in the 2θ range studied. At ambient pressure $CsAuCl_3$ is tetragonal, I4/*mmm*, and the values of a_0 and c_0 from X-ray diffraction are 7.495 and 10.880 Å. From the scans with and without the pressure cell we identified three main peaks due to $CsAuCl_3$ and followed them at 1, 20, and 28 kbar, the last being the upper limit for the cell. The peak at 13.15° is a composite of (002) and (110) but calculation of the structure factors indicates that it is dominated by (110). The other identifiable peaks are (202,022) and (004). By monitoring (004) we can, therefore, follow the variation of c_0 with pressure, while from (110) we can find a_0. The values obtained can then be checked by calculating the position of (202,022) and comparing it with that observed.

The results are shown in Table I, and the (110), (202,022), and (004) reflections at 1 and 28 kbar are shown in Figure 2. Both a_0 and c_0 decrease with increasing pressure. In fact the ratio $2^{1/2}a_0/c_0$ remains remarkably constant: at 0, 1, 20, and 28 kbar it takes the values 0.983, 0.982, 0.984, and 0.986, respectively. At the same time the volume of the unit cell decreases to 99.4, 94.0, and 92.2% of its volume at ambient pressure. The unit cell of the ideal cubic perovskite structure shown in Figure 1 corresponds to a ratio $2^{1/2}a_0/c_0$ equal to 1.0, so it is clear that over the pressure range we have been able to study no transformation to this structure has taken place. On the other hand, the conductivity data[6] suggest a smoothly continuous increase throughout the range, from a room-

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