which allows the immediate rearrangement of an initially formed CN-dihapto keteneimmonium derivative.

The manganese carbonyl system is unique in forming as stable products both the CN-dihapto cyclic acyl derivatives (C in Scheme I) and the 2-azabutadiene derivatives (F in Scheme I). Isomerization of A or B to C (Scheme I) requires rupture of a metal-carbon bond. Furthermore, conversion of C to F requires both the rupture of two metal-carbon bonds and hydrogen migration on the organic ligand. The anomalies in the manganese carbonyl system may therefore be attributed to the lability of their carbonyl groups relative to corresponding rhenium carbonyl or cyclopentadienylmetal carbonyl derivatives and to an unusually high mobility of appropriate ligand hydrogen atoms when the ligand is bonded to a manganese carbonyl unit.

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Crystal and Molecular Structure of Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV). A Square Antiprismatic M(bidentate)$_4$ Stereoisomer[1]

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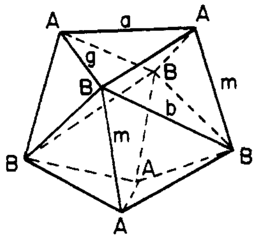
Abstract: The crystal and molecular structure of tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV), Nb(dpm)$_4$, has been determined by the use of three-dimensional X-ray crystallographic methods. A set of 3396 independent reflections with intensities $\gtrsim 4\sigma(I)$ was used in the solution of the structure. The compound crystallizes in the monoclinic space group $P2/c$ with four molecules in a unit cell of dimensions $a = 22.276$ (2) Å, $b = 11.867$ (1) Å, $c = 19.571$ (2) Å, and $\beta = 107.40$ (1)°. Least-squares refinement of positional and anisotropic thermal parameters for all atoms except the hydrogen atoms of two half-molecules located on independent twofold rotation axes terminated in a conventional residual of 0.067. Niobium achieves discrete eight-coordination by bonding exclusively to the oxygen atoms of four dpm ligands. The coordination polyhedron is unequivocally a square antiprism, and the four bidentates span lateral (l) edges. The idealized $D_4(llll)$ square antiprismatic structure resembles a four-bladed propeller and represents a new stereoisomer for an M(bidentate)$_4$ complex.

The D_{2d} dodecahedron (I) and the D_{4d} square antiprism (II) are the two most commonly observed coordination polyhedra for discrete, eight-coordinate complexes.[2-4] In the case of an M(bidentate)$_4$ complex, I can give rise to six different stereoisomers and II can result in three isomers, depending on which set of polyhedron edges[5] are spanned by the ligands. In an early definitive study of eight-coordination, Hoard and Silverton[2] concluded that for identical bidentates the isomers most likely to be observed are those in which the ligands span equivalent polyhedron edges, namely, the dodecahedral $D_{2d}(mmmm)$, $D_2(gggg)$, and $S_4(gggg)$ isomers and the square antiprismatic $D_2(ssss)$ and $D_4(llll)$ structures. Among these, all have been observed[6-17] except the last structure, which resembles a four-bladed propeller.



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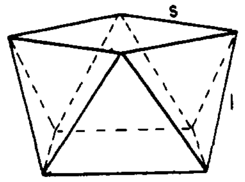

II

In the course of investigating the coordination chemistry of niobium β-diketonates, we observed electron spin resonance spectra for Nb(dpm)$_4$, where dpm is the 2,2,6,6-tetramethyl-3,5-heptanedionate ion $(CH_3)_3CCOCHCOC(CH_3)_3^-$ (sometimes called dipivaloylmethanate), which indicated the complex is square antiprismatic. In addition, X-ray powder diffraction patterns revealed that Nb(dpm)$_4$ is not isomorphous with Zr(dpm)$_4$. Since the latter complex is expected to adopt a D_2(*ssss*) structure analogous to Zr(acac)$_4$,[14] the lack of isomorphism between the niobium and zirconium dpm complexes raised the possibility of a D_4(*llll*) structure existing for Nb(dpm)$_4$. This prompted us to undertake an X-ray crystallographic structure determination of its molecular structure.

Experimental Section

Preliminary examinations of Nb(dpm)$_4$ crystals, which were obtained by slow cooling of a hot benzene-acetonitrile solution, revealed the crystal system to be monoclinic. The systematic absences of reflections ($h0l$, $l = 2n + 1$) were found to be consistent with the space groups *Pc* or *P*2/*c*. The lattice parameters of the crystals were obtained from the least-squares refinement of the diffractometer angles for 12 reflections (a = 22.276 (2), b = 11.867 (1), c = 19.571 (2) Å; β = 107.40 (1)°). The calculated density and the density observed by flotation methods were the same, 1.12 g cm^{-1}, which corresponds to four molecules per unit cell.

The three-dimensional intensity data collection of Nb(dpm)$_4$ was carried out with Cu Kα radiation (λ 1.5418 Å) using a Picker four-circle diffractometer controlled by a Digital Equipment Corp (DEC) 8K PDP-8 computer (FACS-I System) coupled to a DEC 32K disk file and an Ampex TMZ 7-track tape transport. Intensities of reflections were measured by a wandering ω-step-scan procedure[18,19] utilizing a balanced Ross filter pair (Ni/Co) and a crystal-detector distance of 60 cm (He tunnel). The step scan was performed in 0.03° increments of the ω angle, and it extended ±0.075° on either side of the calculated position. Each step was measured for a duration of 4 sec, and the four largest measurements were summed to give the intensity of the reflection.[18] When the observed peak position did not coincide with the calculated ω value, one or two additional steps were taken to assure centering of the scan in the detector window. The background was measured with a Co filter at the ω value of the maximum intensity for a time interval of 4 sec, and this count was multiplied by four to give the background intensity. Finally, since the step-scan procedure is essentially a stationary crystal–stationary counter measurement, in order to avoid Kα splitting effects, the intensity data collection was confined to the range $2\theta < 100°$.

During the intensity data collection, the alignment of the crystal was monitored by measuring the intensities of three appropriate reflections. The program which controlled the intensity data collection also had the capability of "realigning" the crystal automatically by obtaining an orientation matrix for the crystal in its moved position.[19] The need for realignment is based on the intensities of the standard reflections, but since none of these deviated the 10% specified for realignment, no new orientation matrix calculation was performed during the data collection (total time and X-ray exposure ~60 hr). The intensities of the monitored reflections showed only random variations that were well within 3σ of the counting statistics.

The intensities were corrected for absorption using a semiempirical method based on the variation of the relative transmission with azimuthal angle.[20] The linear absorption coefficient was 24.4 cm^{-1}. The maximum observed absorption ratio (I_{max}/I_{min}) was 1.18, applicable to the lower order data, and 1.00 for the higher order reflections. In addition, the intensities were corrected with an empirical correction for a small lack of balance in the Ni/Co filter pair. Finally, Lorentz and polarization factors were applied to convert them to relative structure amplitudes. Of the 5138 independent reflections measured, 3396 were taken to be observable ($>4\sigma(I)$). The latter were used in the solution and the refinement of the structure.

Structure Analysis. The solution of the structure was accomplished by the heavy atom method. Niobium atom positions were obtained from a three-dimensional Patterson map. An electron density map, which was calculated with the phase angles of Nb atom positions on each of the twofold rotation axes of *P*2/*c*, revealed the skeletons of each half-molecule in the asymmetric unit.[21] A subsequent Fourier located the remaining *tert*-butyl carbon atoms to complete the structure.

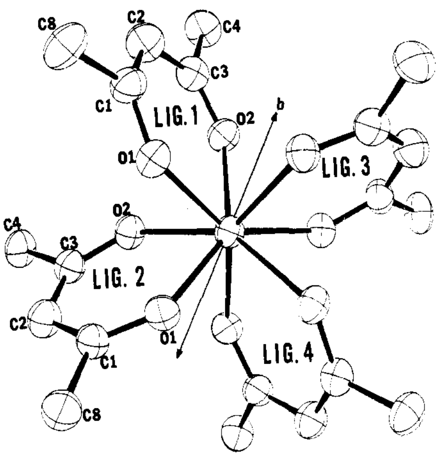

Figure 1. View of molecule A approximately perpendicular to the square faces of the idealized square antiprism. Methyl carbon atoms C5–C7 and C9–C11 of the *t*-C_4H_9 groups have been omitted for clarity. The coordinates of atoms in ligands 3 and 4 are related to those of 1 and 2 by the twofold rotation axis *b* which passes through the center of the Nb atom.

Block-diagonal, unit weight least-squares refinement of positions and isotropic temperature factors gave, after 12 cycles, an *R* value of 0.11 where

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

In the initial stages of the anisotropic refinement the methyl carbon atoms were refined isotropically while the remaining atoms, including the central *tert*-butyl carbons, were refined anisotropically. After six cycles of refinement, *R* reduced to 0.098. An additional ten cycles of unit weight least-squares calculations, where all positional parameters, all anisotropic temperature factors, and an overall scale factor were varied, served to complete the refinement procedure at R = 0.067. The error of fit was 3.99. Shifts in the final cycle of refinement were less than 0.5σ for all parameters. A final difference density map contained only a randomly fluctuating background below 0.6 e/Å^3, except in the vicinity of the niobium positions and occasionally near one of the *tert*-butyl groups. Difference electron density maps were inspected throughout in the *tert*-butyl groups because of the large thermal parameters that were derived for them in the refinement. No disorder was detected, but the syntheses did suggest large anisotropic thermal motions in the area of these atoms. Hydrogen atoms were not included in any of the calculations. Atomic scattering factors used were those of Cromer and Waber.[22] The real part of the anomalous dispersion corrections[23] for Nb was included in the structure factor calculations. Calculations were performed on a Control Data Corporation 6500 computer. Structure factor and least-squares calculations were done with a modified version of BDLS by Sparks and Trueblood (1964). All Fourier computations were performed with RFOUR (Rao, 1966). Molecular geometry calculations were done with DAESD (Harris and Harker, 1963) and PLANE (Harris and Harker, 1965).

Results

The crystal structure of Nb(dpm)$_4$ consists of two independent half-molecules situated on the crystallographic twofold rotation axes of the space group *P*2/*c*. A view of molecule A emphasizing the four-bladed propeller geometry is shown in Figure 1 along with the labeling scheme used to designate atoms in the two symmetry-independent ligands 1 and 2. The same labeling scheme applies to molecule B. A stereoscopic view of molecule A is shown in Figure 2.

Final atomic coordinates and thermal parameters are given in Tables I and II, respectively. The quoted estimated standard deviations were calculated from the inverse matrices of the final least-squares cycle (R = 0.067). Bond

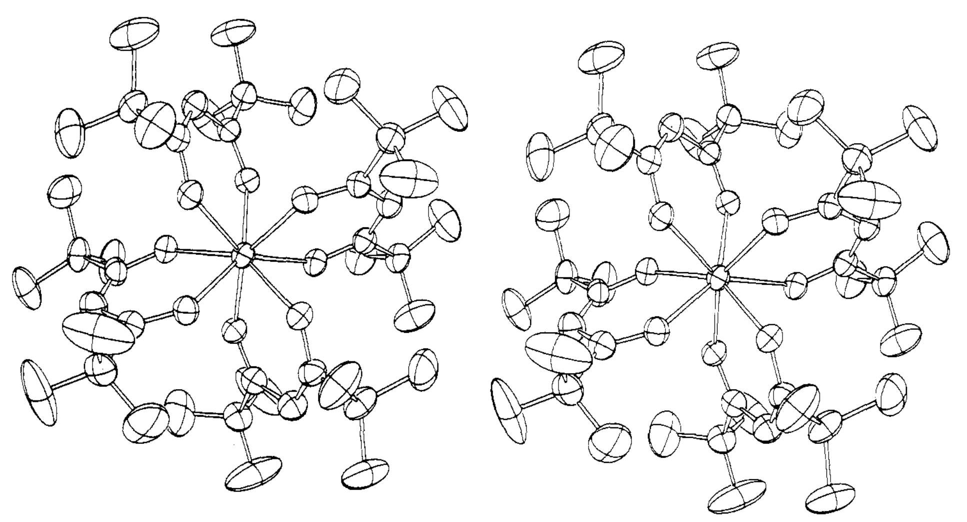

Figure 2. A stereoscopic view of $Nb(dpm)_4$, molecule A.

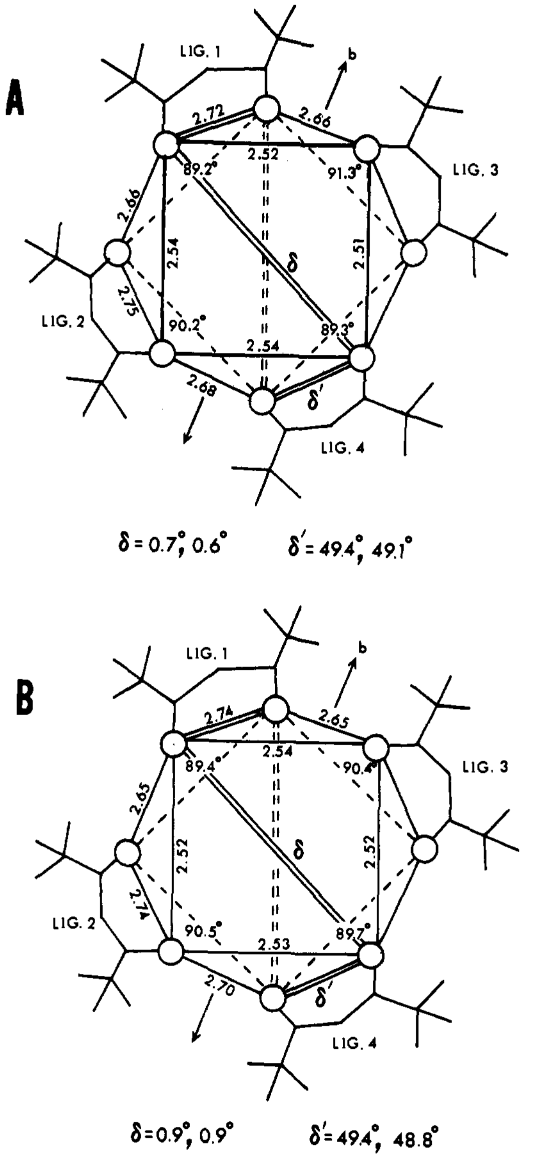

Figure 3. Shape parameters and dimensions of the coordination polyhedra for molecules A and B. Estimated standard deviations for all lengths and angles are 0.01 Å and 0.5°, respectively. The double polyhedron edges identify the symmetry-independent sets of adjacent faces that define the shape parameters δ and δ' (see text).

lengths and angles are given in Tables III and IV. Shape parameters and dimensions of the idealized $D_4(llll)$ antiprisms are given in Figure 3. See paragraph at end of paper regarding structure factor table.

Discussion

The closely related D_{4d} antiprism and D_{2d} dodecahedron, and the structure intermediate between these, the C_{2v} bicapped trigonal prism, can be explicitly distinguished by angles (δ) that are defined by related triangular faces in the three polyhedra.[24,25] This geometric reaction path description of molecular shape, which has been extended to all x-atom families by Muetterties and Guggenberger,[25] provides a quantitative indication of the degree to which an observed structure deviates from an idealized polytopal form. The symmetry-independent adjacent triangular faces that define the two sets of δ values (δ and δ') for molecules A and B of $Nb(dmp)_4$ are identified by the double polyhedron edges in Figure 3.

The observed δ values of 0.7, 0.6, 49.4, and 49.1° for A and 0.9, 0.9, 49.4 and 49.8° for B compare favorably with values of 0.0, 0.0, 52.4, and 52.4° for an idealized, hard-sphere square antiprism. For a hard sphere dodecahedron and a bicapped trigonal prism, respectively, the δ values are 29.5, 29.5, 29.5, and 29.5° and 0.0, 21.8, 48.2, and 48.2°. Thus, the coordination polyhedron of each $Nb(dpm)_4$ molecule is unequivocally a square antiprism, and the bidentates span lateral (l) edges.

Because the two half-molecules in the asymmetric unit lie on twofold axes, they are required crystallographically to have only C_2 symmetry. Nonetheless, D_4 symmetry is nearly achieved (Figure 3). The standard deviation of the four oxygen atoms from the least-squares planes of the square faces is 0.005 Å in A and 0.007 Å in B. The square faces are essentially parallel, the angle of intersection between them being less than 1°.

The four l edges spanned by the diketonates at 2.72–2.75 Å are ~3% longer than the remaining four lateral edges. Also, the edges defining the square faces (s) are appreciably shorter than the l edges. Hoard and Silverton[2] have found the value of l/s which best minimizes the ligand–ligand repulsive interactions in the antiprism to be 1.057. This "most favored" antiprism is further characterized by a θ value of 57.3°, where θ is the angle between the metal–ligand bonds and the C_4 axis. If the special edges spanned by the diketonates are included in the calculation of l/s for

Table I. Final Atomic Positional Parameters[a]

Atom	10^4x	10^4y	10^4z
Nb-A	0	1304 (1)	2500
Nb-B	5000	4168 (1)	7500
O1-1A	656 (4)	1861 (7)	1970 (4)
O2-1A	412 (4)	2691 (7)	3153 (4)
C1-1A	1041 (6)	2686 (12)	2058 (7)
C2-1A	1171 (7)	3442 (13)	2638 (7)
C3-1A	842 (6)	3394 (12)	3164 (6)
C4-1A	1008 (7)	4257 (13)	3774 (7)
C8-1A	1408 (6)	2753 (14)	1488 (7)
O1-2A	183 (4)	−94 (7)	1908 (4)
O2-2A	888 (3)	763 (7)	3205 (4)
C1-2A	624 (6)	−813 (11)	2021 (7)
C2-2A	1158 (6)	−856 (12)	2630 (7)
C3-2A	1253 (6)	−66 (11)	3193 (6)
C4-2A	1851 (6)	−131 (13)	3828 (7)
C8-2A	535 (6)	−1691 (12)	1403 (7)
O1-1B	4422 (3)	4713 (7)	3138 (4)
O2-1B	4539 (3)	5568 (7)	6886 (4)
C1-1B	4042 (5)	5531 (11)	8082 (6)
C2-1B	3864 (6)	6335 (12)	7518 (6)
C3-1B	4136 (6)	6291 (10)	6953 (6)
C4-1B	3920 (7)	7159 (11)	6345 (6)
C8-1B	3722 (6)	5582 (13)	8700 (6)
O1-2B	4885 (4)	2773 (6)	8139 (4)
O2-2B	4085 (3)	3626 (7)	6900 (4)
C1-2B	4453 (6)	2056 (10)	8081 (6)
C2-2B	3892 (6)	2008 (12)	7520 (6)
C3-2B	3734 (5)	2803 (11)	6949 (6)
C4-2B	3103 (6)	2729 (13)	6369 (6)
C8-2B	4583 (7)	1196 (12)	8694 (7)
C5-1A	415 (10)	4731 (22)	3819 (13)
C6-1A	1431 (13)	5126 (24)	3732 (13)
C7-1A	1284 (15)	3640 (20)	4423 (10)
C9-1A	1760 (10)	3830 (16)	1531 (10)
C10-1A	942 (8)	2604 (21)	777 (8)
C11-1A	1871 (9)	1728 (18)	1652 (10)
C5-2A	2274 (8)	0791 (19)	3759 (9)
C6-2A	1670 (8)	0092 (19)	4512 (8)
C7-2A	2154 (9)	−1273 (18)	3891 (10)
C9-2A	−152 (8)	−2078 (17)	1177 (10)
C10-2A	694 (13)	−1056 (18)	806 (11)
C11-2A	978 (9)	−2702 (17)	1595 (10)
C5-1B	4494 (9)	7436 (18)	6092 (11)
C6-1B	3643 (9)	8217 (14)	6536 (9)
C7-1B	3428 (10)	6594 (17)	5751 (9)
C9-1B	4258 (7)	5458 (17)	9406 (6)
C10-1B	3384 (9)	6682 (16)	8706 (8)
C11-1B	3278 (8)	4577 (17)	8584 (8)
C5-2B	3230 (7)	2916 (21)	5643 (7)
C6-2B	2687 (7)	3659 (15)	6512 (8)
C7-2B	2792 (8)	1551 (16)	6358 (9)
C9-2B	5201 (13)	0716 (24)	8817 (15)
C10-2B	4628 (21)	1742 (21)	9323 (11)
C11-2B	4157 (12)	0277 (22)	8588 (13)

[a] The numbers in parentheses in this and other tables are the estimated standard deviations in the least significant digits.

$Nb(dpm)_4$, we obtain an average value of 1.07, if excluded, 1.03. The analogous θ parameter, as defined by the Nb–O bonds and the axis passing through Nb and the center of the square faces, is 57.0 ± 0.4°. Thus the most favored antiprism of Hoard and Silverton is nearly achieved.

Within the level of significance suggested by the standard deviations, the OCCCO portions of the diketonate rings are symmetric and planar. The average C–O, C(ring)–C(ring), and C(ring)–C(aliphatic) distances and internal angles (cf., Tables III and IV) are in the ranges found for previous metal dpm structures.[26–31] The standard deviations of distances from the least-squares OCCCO planes are 0.020 and 0.008 Å for the nonequivalent rings in A and 0.010 and 0.007 Å for those in B.

Metal diketonates often exhibit appreciable folding of the chelate rings about the intra-ring C–O axis. Although this feature is common, it is not essential as no ring folding occurs in $Zn(dpm)_2$[26] and $Ni(dpm)_2$[27] or in the chelate rings which span *l* edges in square antiprismatic $Eu(dpm)_3(C_5H_5N)_2$[32] and $Ho(dpm)_3(C_6H_7N)_2$.[33] Similarly, little or no ring folding occurs in $Nb(dpm)_4$. The smallest dihedral angle observed between OCCCO and ONbO planes is 177.5°, and this corresponds to an out-of-plane Nb distance of only 0.07 Å.

The average C–CH_3 distance is 1.50 ± 0.05 Å, and the average CH_3CCH_3 angle is 109 ± 3°. Because of thermal motion of the *t*-C_4H_9 groups, which is indicated by the large thermal parameters and smaller peak heights for the methyl carbon atoms, the methyl carbon positions are rather poorly determined.

The average intra-ring O–O distance or "bite" of the diketonate ring is 2.74 Å, as compared with 2.74 Å for seven-coordinate $Dy(dpm)_3H_2O$[29] and $Lu(dpm)_3(C_6H_7N)$[31] and eight-coordinate $Eu(dpm)_3(C_5H_5N)_2$,[32] 2.83 Å for dimeric $[Pr(dpm)_3]_2$,[28] 2.71 Å for $Ho(dpm)_3(C_6H_7N)_2$,[33] 2.67 Å for trigonal prismatic $Er(dpm)_3$,[30] and 2.89 Å for tetrahedral $Zn(dpm)_2$.[26] The 0.22 Å range in the bite of dpm is not surprising in view of the similar variability in ring span exhibited by acetylacetonates of differing metal ion size, oxidation number, and coordination geometry.[34]

Since no niobium β-diketonate structures have been reported previously, the average Nb(IV)–O distance at 2.13 Å is of some interest. The observed bond distance is very near the average Nb(V)–O distances to the chelated oxygen ligands in dodecahedral $Nb(O_2)(C_2O_4)_3{}^{3-}$ (2.13 Å)[35] and pentagonal bipyramidal $NbO(C_2O_4)_3{}^{3-}$ (2.13 Å)[36] and $H_2[NbO(OH)(C_2O_4)_2\text{-}H_2O]$ (2.10 Å).[37]

The adoption by $Nb(dpm)_4$ of the square antiprismatic $D_4(llll)$ structure can be explained on the basis of ligand–ligand repulsive interactions between the donor atoms in the first coordination sphere of the metal atom. Considering such repulsions for the five dodecahedral and square antiprismatic stereoisomers in which the bidentates span equivalent edges, Blight and Kepert[38] have shown that the $D_4(llll)$ isomer is slightly more stable than the $D_2(gggg)$ dodecahedral and $D_2(ssss)$ antiprismatic isomers when the bite of the ligands, normalized with respect to the metal–ligand bond distance, is 1.25. When the normalized bite was increased to 1.30, the $D_4(llll)$ isomer was found to be the *only* stable isomer. The bite observed in $Nb(dpm)_4$ is 1.28.

The agreement between theory and experiment may prompt one to anticipate the four-bladed propeller structure whenever the ligand bite is large. However, Blight and Kepert also point out that ordinary bidentates with large bites should not form discrete M(bidentate)$_4$ complexes as the ligand–ligand repulsions would be lowered even more if the ligands bridged different metal atoms to form polymeric structures. In the case of $Nb(dpm)_4$, polymerization of this type may be disfavored by the steric requirements of the *t*-C_4H_9 groups. Whether discrete $D_4(llll)$ square antiprismatic structures can be obtained with sterically less demanding bidentates remains to be investigated.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-2712.

Table II. Anisotropic Thermal Parameters

Atom	β_{11}[a,b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb-A	30 (0)	117 (2)	38 (1)	0	8 (0)	0
Nb-B	29 (0)	109 (2)	31 (0)	0	9 (0)	0
O1-1A	34 (2)	144 (9)	42 (3)	−7 (2)	12 (1)	−6 (2)
O2-1A	37 (3)	137 (9)	47 (3)	−5 (2)	12 (1)	−3 (2)
C1-1A	33 (4)	136 (15)	59 (6)	−11 (3)	5 (2)	5 (4)
C2-1A	48 (5)	158 (17)	55 (6)	−8 (4)	10 (2)	−12 (4)
C3-1A	42 (4)	137 (15)	44 (5)	1 (3)	8 (2)	2 (3)
C4-1A	53 (5)	155 (17)	52 (6)	−7 (4)	6 (2)	−29 (4)
C8-1A	42 (4)	220 (21)	46 (5)	−26 (4)	19 (2)	−8 (4)
O1-2A	38 (2)	122 (9)	41 (3)	−1 (2)	9 (1)	−10 (2)
O2-2A	32 (2)	150 (10)	41 (3)	−1 (2)	7 (1)	−11 (2)
C1-2A	37 (4)	113 (13)	56 (5)	2 (3)	20 (2)	−0 (3)
C2-2A	36 (4)	161 (16)	48 (5)	0 (3)	8 (2)	−5 (4)
C3-2A	34 (4)	140 (15)	47 (5)	−2 (3)	10 (2)	−2 (3)
C4-2A	31 (4)	183 (18)	46 (5)	6 (3)	−2 (2)	−6 (4)
C8-2A	44 (5)	159 (17)	55 (6)	−7 (4)	15 (2)	−32 (4)
O1-1B	35 (2)	136 (9)	31 (3)	1 (2)	14 (1)	1 (2)
O2-1B	36 (2)	117 (9)	40 (3)	6 (2)	15 (1)	10 (2)
C1-1B	30 (4)	140 (15)	42 (4)	9 (3)	13 (2)	−8 (3)
C2-1B	49 (5)	153 (15)	31 (4)	14 (3)	17 (2)	11 (3)
C3-1B	39 (4)	107 (13)	43 (5)	6 (3)	10 (2)	5 (3)
C4-1B	55 (5)	127 (15)	41 (5)	14 (3)	14 (2)	20 (3)
C8-1B	40 (4)	205 (19)	28 (4)	14 (4)	15 (2)	9 (4)
O1-2B	37 (2)	112 (8)	34 (3)	3 (2)	8 (1)	7 (2)
O2-2B	33 (2)	129 (9)	36 (3)	−0 (2)	11 (1)	6 (2)
C1-2B	41 (4)	108 (13)	42 (5)	−6 (3)	14 (2)	−1 (3)
C2-2B	41 (4)	151 (16)	37 (5)	−5 (3)	8 (2)	5 (3)
C3-2B	32 (4)	137 (14)	41 (5)	−4 (3)	11 (2)	−9 (3)
C4-2B	36 (4)	186 (18)	37 (5)	−16 (3)	2 (2)	0 (4)
C8-2B	61 (6)	140 (16)	41 (5)	2 (4)	10 (2)	24 (4)
C5-1A	78 (9)	359 (40)	156 (16)	12 (8)	26 (5)	−151 (11)
C6-1A	160 (15)	452 (46)	130 (14)	−210 (12)	93 (6)	−164 (11)
C7-1A	203 (19)	241 (30)	59 (8)	65 (10)	−43 (5)	−41 (6)
C9-1A	101 (9)	241 (26)	90 (9)	−88 (6)	60 (4)	−36 (6)
C10-1A	55 (6)	440 (39)	50 (6)	−41 (6)	24 (3)	−0 (6)
C11-1A	67 (7)	269 (28)	109 (11)	23 (6)	55 (4)	18 (7)
C5-2A	56 (6)	330 (33)	70 (8)	−56 (6)	−11 (3)	30 (7)
C6-2A	60 (6)	344 (32)	47 (6)	7 (6)	3 (3)	−3 (6)
C7-2A	75 (8)	267 (29)	83 (9)	70 (6)	−27 (3)	−20 (6)
C9-2A	51 (6)	265 (27)	105 (10)	−32 (5)	17 (3)	−95 (7)
C10-2A	192 (16)	255 (29)	93 (10)	−87 (9)	107 (6)	−62 (7)
C11-2A	81 (8)	222 (26)	101 (10)	70 (6)	−14 (4)	−59 (7)
C5-1B	87 (9)	274 (29)	119 (11)	57 (6)	69 (4)	110 (8)
C6-1B	96 (9)	159 (19)	76 (8)	57 (5)	41 (3)	30 (5)
C7-1B	105 (10)	212 (25)	63 (8)	−15 (6)	−28 (3)	35 (6)
C9-1B	49 (5)	343 (29)	30 (4)	24 (5)	16 (2)	10 (5)
C10-1B	93 (8)	253 (25)	54 (6)	82 (6)	46 (3)	30 (5)
C11-1B	61 (6)	325 (30)	65 (7)	−56 (6)	42 (3)	−31 (6)
C5-2B	43 (5)	469 (40)	37 (5)	−30 (6)	5 (2)	7 (6)
C6-2B	39 (5)	227 (23)	75 (8)	22 (4)	3 (2)	−31 (5)
C7-2B	58 (6)	230 (24)	72 (8)	−51 (5)	−7 (3)	−9 (6)
C9-2B	121 (13)	441 (49)	176 (18)	109 (10)	68 (6)	225 (13)
C10-2B	440 (38)	238 (32)	63 (9)	102 (15)	133 (8)	58 (7)
C11-2B	110 (11)	403 (43)	137 (14)	−138 (9)	−54 (5)	170 (11)

[a] The form of the anisotropic thermal correction is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Values of β_{ij} are × 10^4.

Table III. Bond Distances (Å)

	Molecule A		Molecule B		
Bond	Ligand 1	Ligand 2	Ligand 1	Ligand 2	Av
Nb–O1	2.135 (8)	2.144 (8)	2.144 (7)	2.136 (7)	2.133 (9)
Nb–O2	2.118 (8)	2.132 (8)	2.126 (8)	2.126 (8)	
C1–O1	1.28 (2)	1.27 (2)	1.27 (2)	1.26 (2)	1.27 (1)
C3–O2	1.27 (2)	1.28 (2)	1.28 (2)	1.27 (2)	
C2–C1	1.42 (2)	1.40 (2)	1.41 (2)	1.43 (2)	1.42 (1)
C2–C3	1.41 (2)	1.42 (2)	1.41 (2)	1.42 (2)	
C1–C8	1.57 (2)	1.56 (2)	1.57 (2)	1.53 (2)	1.54 (2)
C3–C4	1.53 (2)	1.53 (2)	1.54 (2)	1.52 (2)	
C4–C5	1.46 (3)	1.48 (2)	1.54 (3)	1.54 (2)	1.50 (5)
C4–C6	1.42 (3)	1.53 (2)	1.50 (2)	1.52 (2)	
C4–C7	1.44 (2)	1.50 (3)	1.50 (2)	1.56 (2)	
C8–C9	1.49 (3)	1.53 (2)	1.54 (2)	1.44 (3)	
C8–C10	1.48 (2)	1.52 (3)	1.51 (2)	1.37 (2)	
C8–C11	1.57 (3)	1.53 (2)	1.52 (2)	1.42 (3)	

Table IV. Bond Angles (deg)

	Molecule A		Molecule B		
Angle	Ligand 1	Ligand 2	Ligand 1	Ligand 2	Av
O1–Nb–O2	79.4 (3)	80.0 (3)	79.7 (3)	79.9 (3)	79.8 (3)
Nb–O1–C1	134.5 (8)	133.8 (8)	133.0 (7)	133.7 (7)	134.1 (7)
Nb–O2–C3	135.3 (8)	133.4 (7)	134.6 (7)	134.4 (7)	
O1–C1–C2	124 (1)	126 (1)	127 (1)	125 (1)	125 (1)
O2–C3–C2	124 (1)	125 (1)	126 (1)	124 (1)	
O1–C1–C8	115 (1)	115 (1)	114 (1)	115 (1)	115 (1)
O2–C3–C4	117 (1)	114 (1)	116 (1)	116 (1)	
C1–C2–C3	122 (1)	122 (1)	120 (1)	123 (1)	122 (1)
C2–C1–C8	121 (1)	121 (1)	119 (1)	120 (1)	120 (1)
C2–C3–C4	119 (1)	119 (1)	118 (1)	120 (1)	
C1–C8–C9	112 (1)	108 (1)	106 (1)	110 (1)	109 (4)
C1–C8–C10	107 (1)	105 (1)	112 (1)	110 (1)	
C1–C8–C11	105 (1)	114 (1)	106 (1)	116 (1)	
C3–C4–C7	107 (1)	112 (1)	107 (1)	112 (1)	
C3–C4–C6	117 (2)	108 (1)	115 (1)	107 (1)	
C3–C4–C5	107 (1)	108 (1)	107 (1)	107 (1)	
C5–C4–C6	111 (2)	107 (1)	110 (1)	111 (1)	109 (2)
C5–C4–C7	107 (2)	113 (1)	108 (1)	109 (1)	
C6–C4–C7	108 (1)	108 (1)	109 (1)	111 (1)	
C9–C8–C10	107 (1)	112 (1)	109 (1)	103 (2)	
C9–C8–C11	112 (1)	110 (1)	111 (1)	107 (2)	
C10–C8–C11	110 (1)	107 (2)	112 (1)	111 (2)	

References and Notes

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(5) *The labeling of polyhedron edges* in I and II *follows the notation* of Hoard and Silverton.[2]

(6) Among the numerous tetrakis chelates that adopt the dodecahedral D_{2d}(*mmmm*) structure are $Fe(C_8H_6N_2)_4{}^{2+}$,[7] $Ti(NO_3)_4$,[8] $Zr(C_2O_4)_4{}^{4-}$,[9] and $W(C_9H_5NOBr)_4 \cdot C_6H_6$.[10] The D_2(*gggg*) geometry is adopted by $Th(S_2CNEt_2)_4$,[11] $Pr(tta)_4{}^-$,[12] and $Y(hfac)_4{}^-$,[13] where tta = thenoyltrifluoroacetonate and hfac = hexafluoroacetylacetonate. The tetrakis acetylacetonates of zirconium,[14] cerium,[15] and thorium[16] possess the square antiprismatic D_2(*ssss*) structure. One example exists for the dodecahedral S_4(*gggg*) geometry, $Zr(OC_6H_4CH{=}NC_2H_5)_4$.[17]

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