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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

Variable Stereochemistry of the Eight-Coordinate Tetrakis(oxalato)niobium(IV), $Nb(C_2O_4)_4^{4-}$

F. A. Cotton,* Michael P. Diebold, and W. J. Roth

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The crystallographic analysis of two salts of the $Nb(C_2O_4)_4^{4-}$ anion, A^{4-}, of the formulas $K_2(H_3NCH_2CH_2NH_3)A\cdot 4H_2O$ (**1**) and $K_4A\cdot 3H_2O$ (**2**), showed that A^{4-} can be either square antiprismatic (SA) or dodecahedral (DOD) in the solid state. **1** crystallizes in the triclinic system, $P\bar{1}$, with $a = 7.446$ (1) Å, $b = 17.263$ (4) Å, $c = 18.347$ (4) Å, $\alpha = 111.80$ (2)°, $\beta = 92.33$ (1)°, $\gamma = 90.76$ (1)°, $V = 2187$ (2) Å^3, and $Z = 4$. **2** has a monoclinic cell, $P2_1/n$, with $a = 8.262$ (3) Å, $b = 15.696$ (4) Å, $c = 33.933$ (10) Å, $\beta = 94.67$ (3)°, $V = 4386$ (4) Å^3, and $Z = 8$. For the two pairs of crystallographically independent anions, several criteria were used to assign the SA geometry to three of them and DOD to one. The latter is very similar to the $Zr(C_2O_4)_4^{4-}$ ion. It is postulated that different geometries might be adopted in response to the type of counterion (spherical inorganic or flexible organic cations) with which the complex anion is packed.

Introduction

We report here crystallographic analyses of two compounds containing two $Nb(C_2O_4)_4^{4-}$ ions each, which show that this eight-coordinate Nb(IV) complex can adopt distinctly different geometries in the solid state. All four structures are intermediate between ideal square antiprismatic and dodecahedral, but three of them are close to the former geometry while one approaches the latter. Various aspects of eight-coordination have been extensively analyzed,[1,2] but the proven existence of a complex ion in different geometric forms is very rare. We are aware of only one such case, which was found among the $M(CN)_8^{n-}$ ions (M = Mo, W; n = 3, 4).[3]

Results and Discussion

The tetrakis(oxalato)niobium(IV) anion was isolated as the $K_2(H_3NCH_2CH_2NH_3)[Nb(C_2O_4)_4]\cdot 4H_2O$ (**1**) and $K_4[Nb(C_2O_4)_4]\cdot 3H_2O$ (**2**) salts. They were obtained in connection with the study of the recently reported[4] green aquo ion of low-valent niobium, **3**. Since the direct identification of aquo species is often impossible we attempted to determine the composition of **3** by the study of its derivatives. Accordingly the Nb–aquo ion was reacted with various coordinating species such as SCN^-, $C_2O_4^{2-}$, etc., but it showed rather complex chemistry, which included redox processes. The initial findings indicate that **3** is a precursor to a variety of compounds of the types well recognized for other transition metals but unknown for Nb or Ta. For example, its SCN^- derivatives include trinuclear $Nb_3(\mu_3\text{-}S)(\mu_2\text{-}O)_3(NCS)_9^{6-}$ and the monomeric Nb(IV) complex $Nb(NCS)_4(OMe)_2^{2-}$. The latter as well as $Nb(C_2O_4)_4^{4-}$ were isolated from solutions stored for several weeks, indicating that primary derivatives of **3** undergo slow conversion to Nb(IV) species.

The atomic positional parameters for **1** and **2** are presented in Tables II and III, respectively. In each compound the asymmetric units contain two independent $Nb(C_2O_4)_4^{4-}$ anions. In the following discussion the pair in **1** will be referred to as I and II (primed atoms) and in **2** as III and IV (primed atoms). The Nb–O distances are uniform in all the compounds and vary within a narrow range 2.10–2.17 Å (see Table IV). The O–Nb–O angles for the chelating oxalate ligands are between 70.7 and 73.3°.

Table I. Crystal Data for **1** and **2**

formula	$NbK_2O_{20}N_2C_{10}H_{18}$	$NbK_4O_{19}C_8H_6$
fw	657.37	655.45
space group	$P\bar{1}$	$P2_1/n$
syst absences		$0k0$, $k \neq 2n$; $h0l$, $h + l \neq 2n$
a, Å	7.446 (1)	8.262 (3)
b, Å	17.263 (4)	15.696 (4)
c, Å	18.347 (4)	33.933 (10)
α, deg	111.80 (2)	90.0
β, deg	92.33 (1)	94.67 (3)
γ, deg	90.76 (1)	90.0
V, Å^3	2187 (2)	4386 (4)
Z	4	8
d_{calcd}, g/cm^3	1.997	1.985
cryst size, mm	0.3 × 0.3 × 0.2	0.4 × 0.08 × 0.05
μ(Mo Kα), cm^{-1}	10.033	123.58
data col instrument	P3	RIGAKU
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	Cu Kα (λ = 1.5405 Å)
orientation reflcns no.; range (2θ), deg	25; 17.44–34.82	25; 10.45–20.56
temp, °C	22	22
scan method	ω–2θ	ω–2θ
data col range, deg	$4 \leq 2\theta \leq 50$	$5 \leq 2\theta \leq 120$
unique data: total no.; no. with $F_o^2 > 3\sigma(F_o^2)$	5345; 3922	4914; 2749
no. of params refined	551	466
R^a	0.042	0.067
$R_w{}^b$	0.055	0.083
quality-of-fit indicator^c	1.155	1.731
largest shift/esd, final cycle	0.07	0.17
largest peak, e/Å^3	0.695	1.19^d

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$. [d] Located around metal atom.

The drawings of the anion shown in Figure 1 are representative for all four molecules, and the same atom numbering scheme applies to all cases. In order to determine geometry of the anions both square-antiprismatic (SA) and dodecahedral (DOD) models were considered. The oxygen atoms bound to Nb in the former should define two parallel basal planes and in the latter two perpendicular trapezoids. Appropriate least-squares planes were calculated, and the deviations from both models, expressed in terms of distances of oxygen atoms from these planes, are summarized in Table V. It is evident that no ion conforms rigorously to any ideal geometry but I–III are similar to each other and close to the SA model. In the case of IV the presence of two essentially planar orthogonal trapezoids suggests a DOD structure. The δ angles for the shape-determining edges were calculated by following the procedure outlined by Muetterties and Guggenberger,[2] and the results are shown in Table VI. Again I–III are shown to be essentially square antiprisms (ideal δ's are 0, 0, 52.4, and

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(2) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

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Table II. Positional and Isotropic Equivalent Displacement Parameters for **1**[a]

atom	x	y	z	B, Å^2
Nb(1)	0.0968 (1)	0.28074 (4)	0.32225 (4)	1.61 (1)
O(1)	−0.1581 (7)	0.2927 (3)	0.2693 (3)	2.3 (1)
O(2)	−0.0387 (7)	0.3768 (3)	0.4081 (3)	2.1 (1)
O(3)	0.0432 (7)	0.2321 (3)	0.4126 (3)	2.2 (1)
O(4)	−0.0084 (7)	0.1552 (3)	0.2647 (3)	2.2 (1)
O(5)	0.1536 (7)	0.3884 (3)	0.2939 (3)	2.1 (1)
O(6)	0.1586 (7)	0.2385 (3)	0.2019 (3)	2.1 (1)
O(7)	0.3256 (7)	0.2029 (3)	0.3139 (3)	2.2 (1)
O(8)	0.2884 (7)	0.3484 (3)	0.4142 (3)	1.9 (1)
O(11)	−0.4191 (8)	0.3579 (3)	0.2853 (3)	3.1 (1)
O(21)	−0.2714 (8)	0.4615 (3)	0.4349 (3)	3.0 (1)
O(31)	−0.0523 (9)	0.1218 (3)	0.4385 (3)	3.4 (1)
O(41)	−0.0888 (9)	0.0354 (3)	0.2755 (3)	3.5 (1)
O(51)	0.1942 (9)	0.4372 (3)	0.1974 (3)	3.7 (1)
O(61)	0.2357 (9)	0.2694 (3)	0.1000 (3)	3.5 (1)
O(71)	0.5919 (8)	0.1886 (3)	0.3688 (4)	3.6 (1)
O(81)	0.5164 (9)	0.3388 (4)	0.4922 (3)	3.4 (1)
C(1)	−0.267 (1)	0.3480 (4)	0.3087 (4)	2.3 (2)
C(2)	−0.192 (1)	0.4018 (4)	0.3913 (4)	2.2 (2)
C(3)	−0.016 (1)	0.1554 (4)	0.3921 (4)	2.1 (2)
C(4)	−0.039 (1)	0.1101 (4)	0.3049 (4)	2.1 (2)
C(5)	0.181 (1)	0.3801 (4)	0.2235 (5)	2.4 (2)
C(6)	0.195 (1)	0.2890 (4)	0.1679 (4)	2.2 (2)
C(7)	0.454 (1)	0.2270 (4)	0.3673 (5)	2.3 (2)
C(8)	0.424 (1)	0.3106 (4)	0.4313 (4)	2.0 (2)
Nb(1)′	0.36159 (9)	0.27574 (4)	0.82608 (4)	1.61 (1)
O(1)′	0.4213 (7)	0.2255 (3)	0.9160 (3)	2.3 (1)
O(2)′	0.4501 (7)	0.1506 (3)	0.7690 (3)	2.1 (1)
O(3)′	0.6087 (7)	0.2889 (3)	0.7742 (3)	2.1 (1)
O(4)′	0.5207 (7)	0.3720 (3)	0.9130 (3)	2.1 (1)
O(5)′	0.1218 (7)	0.1995 (3)	0.8158 (3)	2.2 (1)
O(6)′	0.1896 (7)	0.3450 (3)	0.9158 (3)	2.0 (1)
O(7)′	0.3132 (7)	0.3831 (3)	0.7956 (3)	2.2 (1)
O(8)′	0.2830 (8)	0.2319 (3)	0.7039 (3)	2.3 (1)
O(11)′	0.5182 (9)	0.1164 (3)	0.9420 (3)	3.5 (1)
O(21)′	0.5472 (9)	0.0343 (3)	0.7803 (3)	3.5 (1)
O(31)′	0.8718 (7)	0.3574 (3)	0.7915 (3)	2.9 (1)
O(41)′	0.7544 (8)	0.4609 (3)	0.9376 (3)	2.7 (1)
O(51)′	−0.1331 (8)	0.1849 (3)	0.8704 (4)	3.5 (1)
O(61)′	−0.0342 (8)	0.3397 (3)	0.9896 (3)	2.9 (1)
O(71)′	0.298 (1)	0.4312 (3)	0.6980 (3)	3.7 (1)
O(81)′	0.231 (1)	0.2631 (4)	0.5980 (3)	4.1 (2)
C(1)′	0.478 (1)	0.1512 (4)	0.8970 (4)	2.2 (2)
C(2)′	0.492 (1)	0.1070 (4)	0.8091 (4)	1.9 (2)
C(3)′	0.727 (1)	0.3463 (4)	0.8128 (4)	1.9 (2)
C(4)′	0.667 (1)	0.3991 (4)	0.8953 (4)	1.9 (2)
C(5)′	0.005 (1)	0.2232 (4)	0.8682 (5)	2.3 (2)
C(6)′	0.052 (1)	0.3094 (4)	0.9321 (4)	2.0 (2)
C(7)′	0.295 (1)	0.3748 (4)	0.7236 (5)	2.4 (2)
C(8)′	0.264 (1)	0.2841 (4)	0.6689 (4)	2.3 (2)
K(1)	0.1011 (3)	0.3856 (1)	0.5520 (1)	2.89 (4)
K(2)	0.3932 (3)	0.3866 (1)	0.0564 (1)	2.86 (4)
K(3)	−0.0856 (3)	0.5012 (1)	0.1014 (1)	2.83 (4)
K(4)	0.4006 (3)	0.5020 (1)	0.3969 (1)	3.78 (5)
N(1)	−0.1319 (9)	−0.0656 (4)	0.3612 (4)	2.2 (1)*
N(2)	0.343 (1)	−0.1418 (4)	0.3659 (4)	2.9 (1)*
N(3)	−0.6405 (9)	0.0810 (4)	0.1534 (4)	2.6 (1)*
N(4)	−0.169 (1)	0.1339 (4)	0.1125 (4)	2.8 (1)*
C(11)	0.044 (1)	−0.0807 (5)	0.3980 (5)	2.9 (2)*
C(12)	0.166 (1)	−0.1250 (5)	0.3319 (5)	3.4 (2)*
C(13)	−0.465 (1)	0.1309 (6)	0.1591 (6)	3.9 (2)*
C(14)	−0.336 (1)	0.0805 (5)	0.1022 (5)	2.8 (2)*
O(1W)	0.6811 (9)	0.4241 (4)	0.1631 (4)	3.7 (1)*
O(2W)	−0.161 (1)	0.4137 (4)	0.6584 (4)	4.5 (1)*
O(3W)	−0.3421 (9)	−0.0922 (4)	0.4788 (4)	3.8 (1)*
O(4W)	−0.2583 (9)	0.2402 (4)	0.5497 (4)	4.3 (1)*
O(5W)	0.1416 (8)	0.0959 (4)	0.0239 (3)	3.4 (1)*
O(6W)	−0.2728 (9)	0.2547 (4)	0.0538 (4)	4.1 (1)*
O(7W)	0.0285 (9)	−0.0330 (4)	0.1233 (4)	3.7 (1)*
O(8W)	0.5222 (9)	0.0328 (4)	0.3809 (4)	4.1 (1)*

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

52.4°), with the nonzero value of the first two angles being due to bending of the basal squares along one diagonal. For IV the

Table III. Positional and Isotropic Equivalent Displacement Parameters for **2**[a]

atom	x	y	z	B, Å^2
Nb(1)	0.1152 (2)	0.2471 (1)	0.12358 (5)	2.13 (3)
O(1)	0.226 (2)	0.318 (1)	0.1726 (4)	4.1 (4)
O(2)	−0.072 (2)	0.299 (1)	0.1547 (4)	3.4 (3)
O(3)	−0.005 (2)	0.3329 (9)	0.0817 (4)	3.2 (3)
O(4)	0.294 (2)	0.3225 (9)	0.1001 (4)	3.0 (3)
O(5)	0.092 (2)	0.1524 (9)	0.1679 (4)	3.6 (4)
O(6)	0.346 (2)	0.1916 (9)	0.1365 (4)	2.7 (3)
O(7)	0.159 (1)	0.1838 (8)	0.0704 (4)	2.4 (3)
O(8)	−0.100 (2)	0.1809 (8)	0.1050 (4)	2.7 (3)
O(11)	0.190 (2)	0.405 (1)	0.2254 (4)	5.0 (4)
O(21)	−0.142 (2)	0.374 (1)	0.2069 (5)	5.9 (4)
O(31)	0.020 (2)	0.4358 (9)	0.0358 (4)	3.9 (4)
O(41)	0.357 (2)	0.4335 (9)	0.0599 (4)	3.6 (3)
O(51)	0.214 (2)	0.056 (1)	0.2102 (4)	4.8 (4)
O(61)	0.509 (2)	0.117 (1)	0.1812 (4)	4.4 (4)
O(71)	0.048 (2)	0.105 (1)	0.0190 (4)	4.3 (4)
O(81)	−0.233 (2)	0.098 (1)	0.0595 (4)	4.0 (4)
C(1)	0.137 (3)	0.357 (2)	0.1969 (7)	6.8 (6)*
C(2)	−0.039 (3)	0.344 (2)	0.1870 (7)	6.4 (6)*
C(3)	0.072 (2)	0.386 (1)	0.0613 (6)	5.0 (5)*
C(4)	0.255 (2)	0.384 (1)	0.0742 (6)	4.8 (5)*
C(5)	0.217 (3)	0.110 (1)	0.1844 (6)	5.7 (5)*
C(6)	0.382 (2)	0.139 (1)	0.1665 (6)	5.0 (5)*
C(7)	0.048 (3)	0.144 (1)	0.0511 (6)	5.5 (5)*
C(8)	−0.116 (2)	0.138 (1)	0.0716 (6)	4.8 (5)*
Nb(1)′	−0.2048 (2)	−0.2114 (1)	0.11489 (5)	2.33 (3)
O(1)′	−0.438 (1)	−0.2614 (9)	0.1251 (4)	3.5 (3)
O(2)′	−0.316 (2)	−0.1262 (9)	0.1518 (4)	3.5 (3)
O(3)′	−0.076 (2)	−0.229 (1)	0.1710 (5)	5.7 (5)
O(4)′	−0.165 (2)	−0.3421 (9)	0.1245 (4)	4.0 (4)
O(5)′	−0.326 (2)	−0.1245 (9)	0.0733 (4)	3.3 (3)
O(6)′	−0.271 (2)	−0.2822 (9)	0.0627 (4)	2.7 (3)
O(7)′	0.011 (2)	−0.2290 (8)	0.0857 (4)	3.8 (4)
O(8)′	−0.065 (2)	−0.0985 (9)	0.1232 (4)	3.7 (3)
O(11)′	−0.677 (2)	−0.244 (1)	0.1515 (5)	5.7 (4)
O(21)′	−0.530 (2)	−0.097 (1)	0.1868 (5)	4.7 (4)
O(31)′	0.046 (3)	−0.316 (1)	0.2185 (6)	8.4 (6)
O(41)′	−0.078 (3)	−0.446 (1)	0.1694 (5)	7.8 (6)
O(51)′	−0.446 (2)	−0.105 (1)	0.0114 (4)	3.5 (3)
O(61)′	−0.357 (2)	−0.279 (1)	−0.0007 (5)	5.0 (4)*
O(71)′	0.233 (2)	−0.164 (1)	0.0627 (5)	5.0 (4)
O(81)′	0.149 (2)	−0.021 (1)	0.1058 (5)	6.1 (5)
C(1)′	−0.540 (3)	−0.224 (1)	0.1451 (6)	5.5 (5)*
C(2)′	−0.459 (3)	−0.141 (1)	0.1633 (6)	5.8 (5)*
C(3)′	−0.030 (4)	−0.299 (2)	0.1842 (9)	9.9 (8)*
C(4)′	−0.092 (3)	−0.366 (2)	0.1587 (8)	8.5 (7)*
C(5)′	−0.372 (2)	−0.150 (1)	0.0384 (6)	4.6 (5)*
C(6)′	−0.332 (2)	−0.244 (1)	0.0314 (6)	5.4 (5)*
C(7)′	0.110 (3)	−0.169 (1)	0.0822 (6)	5.8 (5)*
C(8)′	0.067 (3)	−0.084 (1)	0.1056 (6)	5.7 (5)*
K(1)	0.4805 (6)	0.1809 (3)	0.0633 (1)	1.96 (9)
K(2)	0.4744 (7)	−1.0205 (3)	0.7506 (1)	3.0 (1)
K(3)	0.2442 (6)	0.4722 (3)	0.4869 (1)	2.4 (1)
K(4)	0.5013 (6)	0.1096 (3)	0.4491 (2)	3.2 (1)
K(5)	0.4813 (7)	0.4180 (3)	0.9213 (2)	3.7 (1)
K(6)	0.3386 (7)	0.3794 (4)	0.2973 (2)	4.2 (1)
K(7)	0.2746 (7)	0.4536 (3)	0.6513 (2)	3.8 (1)
K(8)	0.5750 (8)	0.3255 (5)	0.1547 (2)	5.5 (2)
O(1W)	0.534 (2)	−1.014 (1)	0.9091 (4)	3.9 (3)*
O(2W)	0.704 (2)	0.512 (1)	0.0228 (5)	5.4 (4)*
O(3W)	0.716 (2)	0.321 (1)	0.9714 (5)	5.0 (4)*
O(4W)	0.654 (2)	0.326 (1)	0.0655 (6)	6.8 (5)*
O(5W)	0.266 (2)	0.098 (1)	0.3809 (5)	6.3 (5)*
O(6W)[b]	0.412 (4)	0.503 (2)	0.849 (1)	5.5 (8)*
O(7W)[b]	0.648 (4)	0.458 (2)	0.273 (1)	5.9 (9)*

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Atoms refined with fractional occupancy equal to $^1/_2$.

δ angles approach those in a dodecahedron (all equal to 29.5°). The values of O–M–O angles and O–O contacts, which are listed in Tables VII and VIII, respectively, show again that the first three niobium oxalates are different from IV, which is structurally

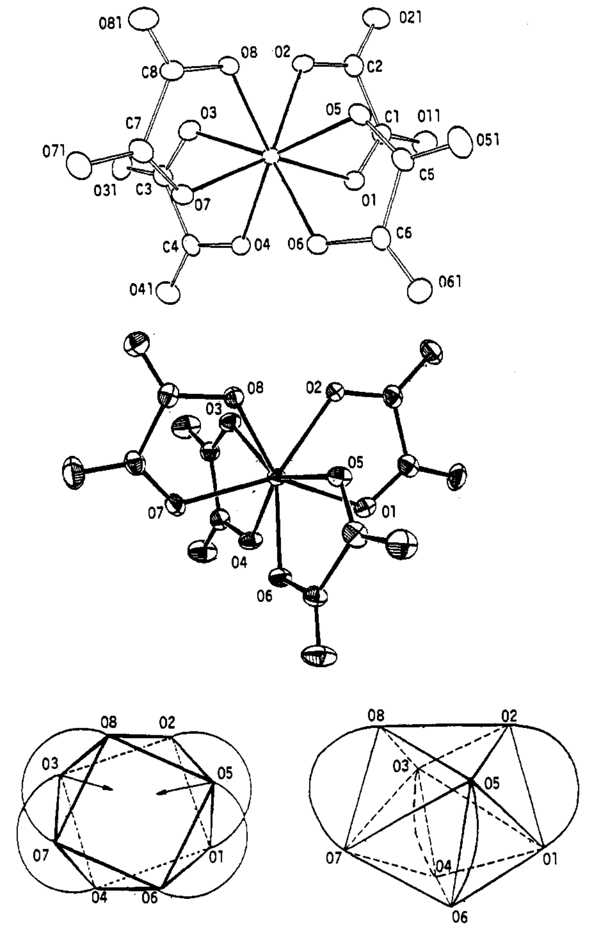

Figure 1. Drawings of the $Nb(C_2O_4)_4^{4-}$ anion. The atom-numbering scheme applies to all four anions, but in the case of II the positional parameters given in Table II correspond to the enantiomorph of the species shown in the figure. The top and middle drawings are ORTEP representations drawn at 30% probability level, and they emphasize apparent SA and DOD geometries, respectively. The bottom pair illustrates schematically the relationship between SA and DOD structures.

Table IV. Nb–O Distances (Å) in the $Nb(C_2O_4)_4^{4-}$ Anions[a]

	I	II	III	IV
Nb(1)–O(1)	2.144 (5)	2.166 (5)	2.138 (14)	2.134 (13)
Nb(1)–O(2)	2.117 (5)	2.148 (5)	2.110 (14)	2.095 (14)
Nb(1)–O(3)	2.166 (5)	2.153 (5)	2.142 (13)	2.12 (2)
Nb(1)–O(4)	2.148 (5)	2.130 (5)	2.100 (13)	2.099 (15)
Nb(1)–O(5)	2.148 (5)	2.163 (5)	2.135 (15)	2.149 (13)
Nb(1)–O(6)	2.125 (5)	2.128 (5)	2.108 (13)	2.123 (12)
Nb(1)–O(7)	2.159 (5)	2.155 (5)	2.118 (13)	2.128 (15)
Nb(1)–O(8)	2.131 (5)	2.136 (5)	2.109 (13)	2.120 (14)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Comparison of Square-Antiprismatic and Dodecahedral Models for $Nb(C_2O_4)_4^{4-}$

	I	II	III	IV
Square Antiprism				
dist of O atoms from basal plane, 10^3 Å	74–141	86–124	109–147	203–266
angle between bases, deg	0.5	0.6	2.1	1.5
Dodecahedron				
dist of O atoms from trapezoid plane, 10^3 Å	162–296	169–302	133–266	52–142
angle between trapezoids, deg	97.4	98.0	96.6	88.3

similar to the dodecahedral $Zr(C_2O_4)_4^{4-}$.[5] As can be seen in Table VIII, distances between vertices of the polyhedra defined by the oxygen atoms bonded to niobium show a characteristic pattern. In the square-antiprismatic structures, I–III, each oxygen atom has four close neighbors (less than 2.82 Å) and three farther away. One of the latter is at a distance of ca. 3.50–3.77 Å, and the remaining two are typically more than 4 Å away, with the shortest separation being 3.94 Å. In IV there are two distinct groups of atoms: one with four short and three long contacts and the second with three short, two intermediate (ca. 3.0 and 3.3 Å), and two long separations. They correspond to A and B sites, respectively, in a dodecahedron. The aforementioned interatomic distances in IV, as well as the four δ angles, match closely those in $Zr(C_2O_4)_4^{4-}$ and both are *mmmm* isomers. The square-antiprismatic species are all *ssss* forms in contrast to the eight-coordinate niobium(IV) dipivaloylmethane complex Nb[*t*-BuC(O)CHC(O)-*t*-Bu]$_4$, which is of the type *llll*.[6]

The relationship between the two forms of $Nb(C_2O_4)_4^{4-}$ is illustrated in Figure 1, which shows idealized polyhedra. Since the number of edges in a square antiprism and a dodecahedron are 16 and 18, respectively, the conversion of the former to the latter requires the creation of two new edges. To the first approximation this takes place by closing of the distances between O(1) and O(3) and between O(5) and O(7). Of course other O–O distances change as well (see Table VI)) due to the rigidity of the oxalate anion and in order to give a uniform distribution of ligands around Nb. It is noteworthy that several eight-coordinate complexes exhibit intermediate structures between *mmmm* and *ssss* geometries.[1]

Since in the solid state there exists strong electrostatic interaction between cations and ligating oxalates as well as hydrogen bonding, it is intuitively evident in this case, as it was for $Mo(CN)_8^{4-}$, that the adoption of different geometries is due to differences in the environments about the anions. However, the number of interactions is enormous and it is virtually impossible to define specific factors that are responsible for the observed phenomenon. Apparently the energy surface containing and connecting dodecahedral and square-antiprismatic geometries is shallow, allowing smooth interconversion between the two forms, and even allowing them to coexist. A similar situation was observed for another eight-coordinate complex of niobium, namely $Nb(CN)_8^{4-}$, which was found to be dodecahedral in the solid state, while its ESR spectrum in solution suggested square-antiprismatic geometry.[7]

In the case of $Mo(CN)_8^{4-}$ the geometry changed in response to the size of the counterion:[3b] DOD for H^+ and Na^+, SA for K^+, and bicapped trigonal prism for Cs^+. However, for the 2-carboxypyridinium salt of $Mo(CN)_8^{4-}$ a DOD structure was established,[3c] and this was postulated as being due to the ability of such a geometry to adopt different M–ligand bond lengths. The present case points to still another factor that may affect such structures, namely shape and flexibility of the counterion. Thus, rigid spherical cations could promote one form, e.g. DOD, while more flexible organic counterions another, e.g. SA.

Experimental Section

All manipulations were performed under an inert atmosphere of argon by using standard vacuum-line/Schlenk glassware techniques. Nonaqueous solvents were purified by conventional methods. Water and hydrochloric acid were deoxygenated by boiling and bubbling of N_2, respectively, $Nb_2Cl_6(THT)_3$ was prepared as described previously.[8] We

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Table VI. Dihedral Angles between Faces of the O_8 Polyhedra in $Nb(C_2O_4)_4^{4-}$ [a,b]

A. Basal Faces[c]

anion	faces 124, 234	143, 123	568, 678	567, 578
I	18.5	$\underline{17.0}$	9.6	$\underline{9.3}$
II	16.2	$\underline{15.1}$	10.8	$\underline{10.4}$
III	14.5	$\underline{13.7}$	19.2	$\underline{17.6}$
IV	28.1	$\underline{24.8}$	35.3	$\underline{29.8}$

B. Side Faces[c]

anion	faces 146, 467	467, 347	347, 378	378, 238	238, 258	258, 125	125, 156	156, 146
I	56.4	52.5	$\underline{49.1}$	50.7	56.6	52.7	$\underline{50.6}$	48.4
II	57.4	52.0	$\underline{51.2}$	48.4	57.1	50.9	$\underline{50.3}$	50.2
III	55.8	51.0	$\underline{49.4}$	52.9	56.2	51.3	$\underline{46.9}$	53.4
IV	57.7	51.8	$\underline{39.4}$	57.0	58.1	53.9	$\underline{43.4}$	54.6

[a] Each triangular face is represented by the numbers of the oxygen atoms defining it. [b] The δ angles for shape-determining edges are underlined. [c] Refers to basal and side faces of the apparent square antiprism.

Table VII. O–M–O Angles in $Nb(C_2O_4)_2^{4-}$ and $Zr(C_2O_4)_4^{4-}$ [a]

	I	II	III	IV	$Zr(C_2O_4)_4^{4-}$
O(1)–Nb(1)–O(2)	73.0 (2)	72.2 (2)	72.2 (5)	72.1 (5)	71.42
O(1)–Nb(1)–O(3)	107.1 (2)	108.5 (2)	109.6 (6)	101.4 (6)	101.33
O(1)–Nb(1)–O(4)	74.9 (2)	76.1 (2)	74.6 (5)	75.3 (6)	74.76
O(1)–Nb(1)–O(5)	79.8 (2)	79.0 (2)	82.5 (6)	87.8 (5)	87.48
O(1)–Nb(1)–O(6)	79.2 (2)	78.2 (2)	74.4 (5)	76.7 (5)	76.26
O(1)–Nb(1)–O(7)	145.5 (2)	148.7 (2)	144.5 (5)	146.1 (5)	144.86
O(1)–Nb(1)–O(8)	142.0 (2)	138.9 (2)	141.5 (5)	140.7 (5)	143.54
O(2)–Nb(1)–O(3)	75.1 (2)	75.0 (2)	76.5 (5)	76.1 (6)	78.27
O(2)–Nb(1)–O(4)	124.2 (2)	123.6 (2)	122.6 (6)	127.0 (6)	127.99
O(2)–Nb(1)–O(5)	76.8 (2)	76.4 (2)	78.8 (6)	77.5 (5)	78.29
O(2)–Nb(1)–O(6)	141.2 (2)	140.2 (2)	138.1 (5)	137.6 (5)	135.89
O(2)–Nb(1)–O(7)	139.6 (2)	137.4 (2)	142.4 (5)	141.8 (5)	143.54
O(2)–Nb(1)–O(8)	72.0 (2)	70.5 (2)	72.9 (5)	69.3 (5)	72.89
O(3)–Nb(1)–O(4)	72.4 (2)	72.5 (2)	72.4 (5)	70.7 (6)	71.00
O(3)–Nb(1)–O(5)	147.4 (2)	146.2 (2)	147.2 (5)	147.7 (6)	150.75
O(3)–Nb(1)–O(6)	140.2 (2)	141.1 (2)	139.5 (5)	138.9 (6)	138.09
O(3)–Nb(1)–O(7)	79.3 (2)	77.9 (2)	80.3 (5)	91.3 (6)	87.48
O(3)–Nb(1)–O(8)	77.4 (2)	77.8 (2)	77.2 (5)	76.5 (6)	78.29
O(4)–Nb(1)–O(5)	138.7 (2)	139.9 (2)	140.1 (5)	141.3 (5)	138.09
O(4)–Nb(1)–O(6)	71.6 (2)	72.2 (2)	70.2 (5)	69.1 (5)	68.04
O(4)–Nb(1)–O(7)	75.1 (2)	76.9 (2)	76.5 (5)	79.6 (6)	76.26
O(4)–Nb(1)–O(8)	138.8 (2)	140.8 (2)	139.9 (5)	136.1 (5)	135.89
O(5)–Nb(1)–O(6)	72.0 (2)	72.2 (2)	72.4 (5)	73.2 (5)	71.00
O(5)–Nb(1)–O(7)	113.5 (2)	113.2 (2)	107.8 (5)	98.1 (5)	101.33
O(5)–Nb(1)–O(8)	78.4 (2)	76.0 (2)	75.2 (5)	77.0 (5)	78.27
O(6)–Nb(1)–O(7)	75.6 (2)	78.6 (2)	76.7 (5)	73.2 (5)	74.76
O(6)–Nb(1)–O(8)	122.1 (2)	122.9 (2)	125.7 (5)	130.4 (5)	127.99
O(7)–Nb(1)–O(8)	72.3 (2)	72.1 (2)	73.3 (5)	72.7 (5)	71.42

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VIII. Oxygen–Oxygen Contacts (Å) in the Coordination Sphere of $Nb(C_2O_4)_4^{4-}$ and $Zr(C_2O_4)_4^{4-}$

	I	II	III	IV	$Zr(C_2O_4)_4^{4-}$
O(1)–O(2)	2.534	2.542	2.503	2.490	2.546
O(1)–O(3)	3.467	3.505	3.498	3.294	3.359
O(1)–O(4)	2.611	2.648	2.569	2.586	2.667
O(1)–O(5)	2.753	2.754	2.818	2.970	3.002
O(1)–O(6)	2.720	2.708	2.566	2.640	2.712
O(1)–O(7)	4.110	4.161	4.053	4.077	4.090
O(1)–O(8)	4.043	4.028	4.010	4.006	4.142
O(2)–O(3)	2.610	2.618	2.633	2.599	2.785
O(2)–O(4)	3.770	3.769	3.692	3.753	4.010
O(2)–O(5)	2.650	2.667	2.694	2.659	2.786
O(2)–O(6)	4.001	4.020	3.939	3.932	4.135
O(2)–O(7)	4.013	4.010	4.002	3.991	4.142
O(2)–O(8)	2.497	2.473	2.508	2.397	2.633
O(3)–O(4)	2.549	2.533	2.504	2.443	2.580
O(3)–O(5)	4.141	4.130	4.103	4.103	4.251
O(3)–O(6)	4.034	4.037	3.988	3.975	4.149
O(3)–O(7)	2.759	2.707	2.747	3.040	3.002
O(3)–O(8)	2.687	2.694	2.651	2.625	2.786
O(4)–O(5)	4.021	4.032	3.981	4.008	4.149
O(4)–O(6)	2.498	2.509	2.418	2.395	2.513
O(4)–O(7)	2.625	2.666	2.611	2.706	2.712
O(4)–O(8)	4.006	4.018	3.955	3.912	4.135
O(5)–O(6)	2.513	2.529	2.507	2.548	2.580
O(5)–O(7)	3.602	3.605	3.437	3.231	3.359
O(5)–O(8)	2.706	2.646	2.589	2.659	2.785
O(6)–O(7)	2.626	2.714	2.623	2.536	2.667
O(6)–O(8)	3.723	3.745	3.752	3.850	4.010
O(7)–O(8)	2.530	2.526	2.522	2.518	2.546

are confident that a combined solvent/pressure dependence study, presently under way in our laboratories, will enable us to differentiate between these two possible transition states.

Preparation. To a slurry of $Nb_2Cl_6(THT)_3$ (0.66 g, 1 mmol) in 20 mL of THF at 0 °C was added 5 mL of concentrated HCl solution. When the mixture had turned green (usually after 0.5 h), it was evaporated to dryness. The solid residue was redissolved in 20 mL of water, affording a green stock solution of the Nb–aquo species, **3**. The addition of $K_2C_2O_4{\cdot}H_2O$ (0.75 g, 5 mmol) precipitated a dark red solid, which was removed by filtration. The remaining red solution was divided in half, and one portion was layered with a 1:1 mixture of water and methanol containing $H_2NCH_2CH_2NH_2{\cdot}2HCl$ and the second with 1:3 water–methanol. After 3–4 weeks dark red needles of **1** and **2**, respectively, were obtained in estimated yields of 20–30%. An improved synthetic procedure is anticipated when we learn more about the nature and chemistry of **3**.

X-ray Crystallography. Single-crystal X-ray analyses of both salts have been carried out by standard procedures, which have been described in detail elsewhere.[9] Relevant crystallographic data are given in Table I.

In both cases the positions of the Nb atoms were derived from a three-dimensional Patterson function. The remaining non-hydrogen atoms were located and refined by a series of least-squares refinements and difference Fourier syntheses. An absorption correction by the method of Walker and Stuart[9c] was applied for **2** after isotropic refinement. Selected atoms in both compounds were assigned anisotropic displacement parameters (see Tables II and III) and the structures refined to convergence. In the case of **2** two water molecules were refined with fractional occupancy $^1/_2$ because of high displacement parameters of the corresponding oxygen atoms. There was also some residual electron density above 1 e Å^{-3} remaining around the Nb atoms.

Tables of anisotropic displacement parameters, full listings of bond distances and angles, and listings of structure factors and relevant least-squares planes for both compounds are provided as a supplementary material.

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Supplementary Material Available: For the crystal structures of **1** and **2**, tables of complete bond distances and angles, anisotropic displacement parameters, least-squares planes for bases in the SA model and trapezoids in the DOD model (19 pages); for both structures, listings of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemical Sciences, University of Catania, 95125 Catania, Italy,
and Department of Inorganic, Organometallic and Analytical Chemistry, University of Padua, 33131 Padova, Italy

Copper(II) Complexes of Diastereoisomeric Methionylmethionines in Aqueous Solution. Favoring of the Amide-Deprotonated Complex in the L,L-Dipeptide without Sulfur Coordination

Raffaele P. Bonomo,[†] Giuseppe Maccarrone,[†] Enrico Rizzarelli,*[†] and Maurizio Vidali*[‡]

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A thermodynamic investigation has been carried out on copper(II) complexes with L-methionyl-L-methionine or D-methionyl-L-methionine at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3). Thermodynamic stereoselectivity has been found in the formation of the amide-deprotonated complexes. In particular, the formation of the copper(II) complex with the L,L-dipeptide is enthalpically favored. Structural information obtained by the EPR spectra in solution parallels the thermodynamic data: a slightly larger copper hyperfine coupling constant has been determined in the case of the copper(II) complex with L-methionyl-L-methionine. Comparison with data previously obtained for similar dipeptides containing noncoordinating side-chain groups evidences that the sulfur atom is not coordinated to the metal ion. The thermodynamic stereoselectivity of the amide-deprotonated complex differences of 0.3 in log β and 1.7 kcal mol^{-1} in $\Delta H°$ can be attributed to the hydrophobic interaction between the residues of side chains. This noncovalent "bonding" is possible only for the L,L-diastereoisomer where the side chains are on the same side of the coordination plane.

Recently, we have studied the formation, stability, and bonding details, in aqueous solution, of copper(II) coordination of some diastereoisomeric dipeptides containing noncoordinating side-chain groups.[1] By means of potentiometric and calorimetric measurements, evidence has been found of thermodynamic stereoselectivity in the formation of the amide-deprotonated complexes. If, on the basis of the EPR parameters, different coordination numbers are excluded when the metal ion is bound to the L,D- and L,L-isomers, the slightly larger stability of the copper(II) L,L-dipeptide complexes compared to that of the analogous L,D-dipeptide ones was attributed to the solvophobic interaction[2] between the side-chain groups. This noncovalent[3] "bonding" is possible only for the L,L-diastereoisomers, because the side chains are on the same side of the coordination plane.

Here we report the results of the thermodynamic studies for the complex formation of copper(II) L,L- or D,L-methionylmethionine peptides in aqueous solution. The aim of this work is to find unambiguous evidence of the possible involvement of sulfur atoms in the bonding to the metal ion and also to assess the role played by the thioether in the stability of the complexes. A small, but reproducible stereoselective effect has been observed in both free energy (0.67 kcal) and enthalpy (0.41 kcal) changes associated with the formation of the bis complexes Ni(D/L-Met)$_2$[4] (Met = methionine) and attributed to the tridentate binding of the amino acid, hypothesizing the existence of weak coordination between Ni^{2+} and the thioether sulfur atom in the Ni(D-Met)(L-Met)complex.

As regards the ligands here investigated, if the sulfur is engaged in the coordination, two apical thioethereal bonds would be possible in the case of the L,D-isomer while one only would be possible in the case of the L,L-peptide. The resulting different coordination numbers of the metal ion could be the reason for the thermodynamic stereoselectivity. Thus, to obtain further information about

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[†] University of Catania.
[‡] University of Padua.

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