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Factors Affecting the Shape of Eight-Coordinate Species. Crystal and Molecular Structure of (NbT4)2(O(H···Cl)3)·CH3CN

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The compound $(NbT_4)_2(O(H\cdots Cl)_3)\cdot CH_3CN$, where $T^- = C_7H_5O_2^-$, crystallizes in the monoclinic space group $C2/c$ with cell constants $a = 15.16$ (1) Å, $b = 13.94$ (1) Å, $c = 25.88$ (2) Å, $\beta = 95.46$ (4)°, and $Z = 8$. Of the 3601 reflections measured by counter methods, 1651 ($>2.3\sigma$) were used in full-matrix least-squares refinement to give a final R factor of 7.5%. The geometry of the eight oxygen atoms coordinated to the niobium (average Nb–O distance 2.088 (5) Å) is best described as an irregular bicapped trigonal prism, distorted toward a dodecahedron. The mean O···O separation in the four tropolonato ligands is 2.432 (17) Å, which is significantly and unexpectedly smaller than the values reported for other tropolonato complexes. The most notable features of the "NbO_8" polyhedron are two interligand O···O contacts which are very short (2.410 (14) and 2.467 (17) Å) compared to other interligand contacts. The "NbO_8" polyhedron appears to be a good example in a pattern of nonimposed short contacts which occur between oxygen atoms whose lone pairs of electrons overlap and where empty valence-shell d orbitals exist on the central metal atom. An interaction involving the lone pairs and the vacant d orbitals is suggested to rationalize these results. The species $(O(H\cdots Cl)_3)^{2-}$ contains the H_3O^+ cation hydrogen bonded to the three chloride ions placed at the corners of the base of a flattened trigonal prism. A twofold axis passes through one of the chloride ions and relates the other two; the oxygen atom is disordered on either side of the twofold axis at the apex of the trigonal prism.

Introduction

In our investigation[1] of the correlation of eight-coordinate geometry with existing theories of high-coordination,[2,3] we have determined the arrangement of the eight oxygen donor atoms about niobium in the NbT_4^+ cation (where $T^- = C_7H_5O_2^-$), originally reported as NbT_4Cl. Calculations to predict the geometry of $M(biden)_4$ (biden = bidentate ligand) complexes on the basis of ligand–ligand repulsions[3] show that the geometry is critically dependent on the parameter b—the ratio of the donor atom separation to the metal–donor atom distance. It was assumed on the basis of previous reports of structures[1,4,5] involving the supposedly rigid tropolonato ligand that the donor atom separation would be constant in the estimation of b for a series of MT_4 complexes. Thus, with a value for the Nb–O distance of 2.05 Å (estimated from Bragg–Slater radii), a substantial change in b and therefore a difference in eight-coordinate geometry between NbT_4^+ and $HScT_4$ (mean Sc–O bond length of 2.21 Å) would be expected.

Experimental Section

$(NbT_4)_2(O(H\cdots Cl)_3)\cdot CH_3CN$ was prepared by the method reported by Muetterties and Wright.[6] Crystals obtained from this preparation were very small, and a compromise between size and quality was necessary in the choice of crystal for investigation. Using copper radiation (λ 1.5418 Å), a Weissenberg photograph of the reciprocal lattice layer $h0l$ and precession photographs of the reciprocal lattice layers $0kl$, $hk0$, hkh, and $hk2h$ were taken. These indicated monoclinic symmetry and showed systematic absences for hkl, $h + k = 2n + 1$, and $h0l$, $l = 2n + 1$, suggesting the monoclinic space groups Cc or $C2/c$. The intensities of even the strongest reflections measured by counter methods were weak, and after considerable effort, a new crystal of approximate dimensions 0.12 × 0.08 × 0.08 mm was found. This crystal was mounted with the c axis approximately parallel to the Φ axis of the diffractometer. In view of the weak-intensity data expected, the interface circuitry on the diffractometer control system was modified to read the units digit on the number of counts for each reflection.

Accurate cell dimensions were determined from counter measurement of 12 of the strongest reflections having $2\theta > 20°$ using a Picker FACS-1 computer-controlled four-circle diffractometer (Mo $K\alpha$ radiation, λ 0.70926 Å), with a takeoff angle of 1.0°.

Crystal Data

$Nb(C_7H_5O_2)_4(O(H\cdots Cl)_3)_{1/2}\cdot{}^1/_2CH_3CN$, formula weight 654.5, crystallizes in the monoclinic space group $C2/c$; $a = 15.16$ (1) Å, $b = 13.94$ (1) Å, $c = 25.88$ (2) Å, $\beta = 95.46$ (4)°, $V = 5444$ Å^{-3}, $Z = 8$, $d_m = 1.57$ (2) g/ml (flotation), $d_x = 1.597$ g/ml, μ(Mo $K\alpha$) = 5.22 cm^{-1}, $T = 22°$C.

Diffraction data were collected using monochromatized molyb-

denum radiation (graphite monochromator, λ(Mo$K\alpha$) 0.70926 Å), with a takeoff angle of 3.0°. Reflections for the unique set of data were collected using a scintillation detector with pulse height analysis, with a symmetrical θ–2θ scan at a speed of 1°/min. For data where $\sin \theta < 0.2164$, a scan base width of 1.2° was used, and for the outer data (0.2164 $< \sin \theta < 0.3827$), a base width of 1.0° was used; separate scales were assigned to the inner and outer shells of data for the purpose of refinement. Background counts of 20 sec were measured at both scan limits. The intensities were corrected for Lorentz and polarization effects; absorption was neglected since it was estimated to produce an extreme error of ±1% in F. A total of 3601 reflections were measured of which 1666 were considered to be observed (i.e., greater than 2.3σ where $\sigma_{I(net)} = [TC + (t_s/t_b)^2(B_1 + B_2) + (kI)^2]^{1/2}$ where TC is the total count, B_1 and B_2 are the background counts at each end of the scan range, t_s is the scan time, t_b is the total background count time, k is a constant set initially to 0.03 (see next section), and I is the net count.

The maximum value of I recorded during data collection was 17,409 for the 113 reflection.

Structure Determination and Refinement

A three-dimensional Patterson synthesis on the inner shell of data ($\sin \theta < 0.2164$) gave the position of the niobium atom and one chlorine atom. These parameters were refined together with a scale factor to give $R = 0.445$, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. A Fourier synthesis gave the eight oxygen atoms bonded to the niobium. Three cycles of refinement using the full set of data and subsequent electron density difference maps gave all of the tropolonato carbon atom positions and 16 of the hydrogen atom positions as well as two prominent peaks on the twofold axis near the chlorine atom and two other peaks (approximately 2.7 Å apart), one of which was on the twofold axis. In the first case, refinement was continued using a model of $(O(H\cdots Cl)_3)^{2-}$ with one chlorine atom on the twofold axis which related the other two chlorine atoms in the species to give the base of a flattened trigonal prism. The oxygen atom formed the apex of this pyramid and was disordered on either side of the twofold axis (this disorder being consistent with the direction of elongation of the peak as observed in the difference map).

The other two peaks were refined as a CH_3CN molecule randomly disordered between two sites on either side of the twofold axis. The peak in the general position was split to give the $-C\equiv N$ group of this molecule, and refinement of this model gave reasonable final atomic coordinates and temperature factors. Although evidence for the H_3O^+ and CH_3CN species was not found from ir spectra, thermogravimetric analysis gave the percent nitrogen as 0.94, compared to a calculated value based on this model of 1.07.

The remaining hydrogen atom positions (excluding those in the H_3O^+ and CH_3 groups) were calculated with a C–H bond length of 0.96 Å, and all hydrogen atoms were assigned temperature factors of 0.038 Å^2, a value based on the refined isotropic temperature factors of the carbon atoms to which they were bonded. An R factor of 0.077
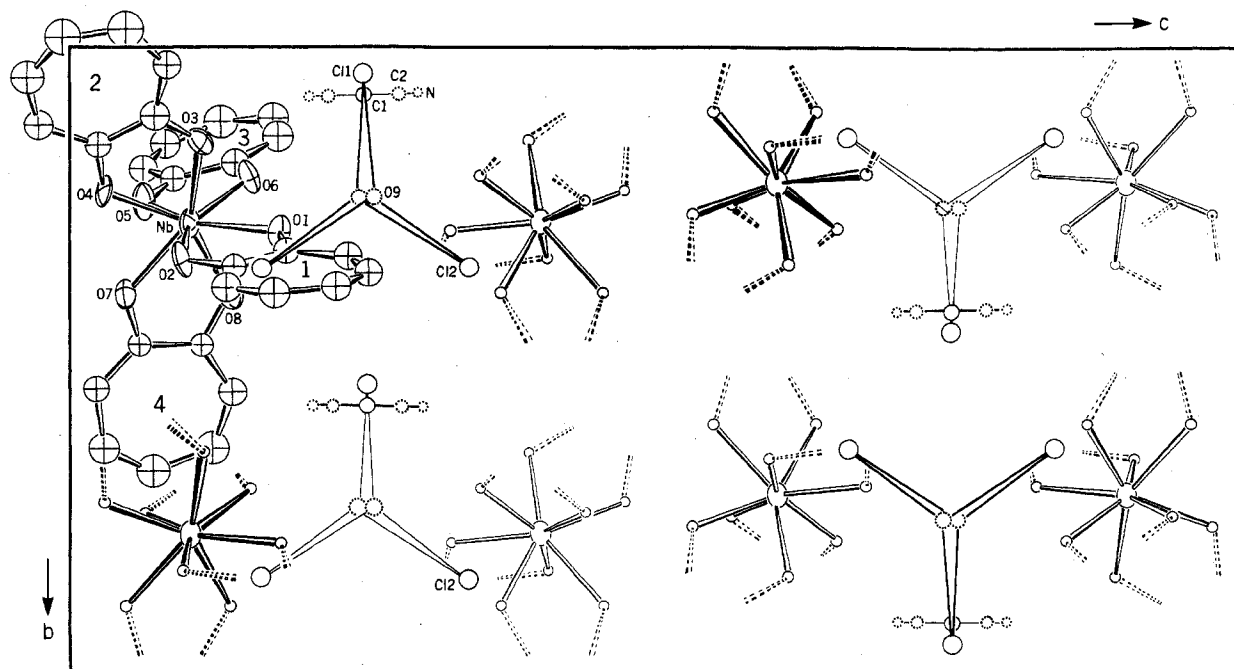
Figure 1. View along the *a* axis of the unit cell of $NbT_4(O(H\cdots Cl)_3)\cdot CH_3CN$. In all but one NbT_4^+ cation, the C_7 tropolonato rings are omitted for clarity. The other cation illustrates the thermal motion ellipsoids (50%) and labeling.

was obtained after refinement of all nonhydrogen atom positional and thermal motion parameters and, with niobium, chlorine, and oxygen atoms (except for O_9 in H_3O^+) allowed, anisotropic thermal motion parameters. The estimated standard deviation (S) of an observation of unit weight was 1.233 given by $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$ (where w are the counterweights $[=1/(\sigma_F)^2]$ given in terms of $\sigma_F = \sigma_I/(Lp)(2F_o)$, and $(m - n)$ is the difference between the number of independent observations and the number of parameters varied).

A listing of the correlation matrix indicated numerous interactions (510 >0.1), although the majority of these were not strong. Geller[7] has pointed out that these coefficients are directly related to the structure model (e.g., the ratio of the number of observations to the number of variables, vector overlap in the Patterson map, etc.), to an incorrect weighting scheme, or to the nature of the atomic scattering factors. It was suspected that the refinement had stopped at some kind of "false minimum". Further evidence for this came from a comparison of the least-squares estimated errors in the tropolonato bond lengths and the errors calculated on the basis of the internal consistency within the model (it was assumed that all the tropolonato ligands were chemically equivalent). Thus, for a group of n chemically similar bond lengths, one can estimate the average standard error using $\sigma_s = (\sum(l_n - \bar{l})^2/(n - 1))^{1/2}$. Values of σ_s calculated in this way were a factor of 2–3 times larger than the corresponding least-squares estimated errors. The tropolonato ligands were therefore chemically equivalent within the errors expressed by values of σ_s but significantly different on the basis of the least-squares estimated errors.

An analysis of $\sum(w\Delta^2/n)$ values indicated systematic trends which showed that the strong and/or low-angle data were heavily overweighted. To achieve an acceptable weighting scheme, it was considered necessary to increase the constant k (in the expression used to calculate $\sigma_{I(net)}$) to down-weight reflections of this type. After some analysis, a value of $k = 0.075$ was determined as appropriate. Refinement was continued using the reprocessed data (1651 observed reflections). Large shifts in the parameters of the tropolonato ligands were observed; the estimated least-squares errors in the bond lengths of the ligands were higher than those in the previous model and generally agreed well within those errors (σ_s) calculated on the basis of internal consistency (which were lower for the new model). The one exception was the $O_1\cdots O_2$ donor atom separation (2.476 (15) Å) which was significantly higher than the values for the other three ligands (mean value 2.418 (8) Å). A final R factor of 0.075, based on the 1651 observed reflections, was obtained. The value of S for the new model was 1.263, and although the increase in this value is recognized, the change of weighting scheme to give an even distribution of $w\Delta^2$ values throughout the data is considered to be of overriding

importance. The correlation matrix still showed some interactions, though fewer than the earlier refinement. In view of these difficulties in refinement, the final model must be interpreted cautiously; it is possible that the weighting scheme has been fitted to a bad model. One method of testing the final model in such a situation is to look for any change in the atomic and thermal parameters when more data are used.[7] One cycle of refinement using the final parameters and the 2344 reflections $>1.0\sigma$, however, gave negligible shifts, indicating that the final model was unchanged when 50% more data were included in the refinement. The value of S for this refinement was 1.290. The possibility that the crystal belongs to the noncentrosymmetric space group Cc was also considered. However the agreement we have obtained indicates that any departure must be small and that any attempt to refine such a model would lead to a prohibitive increase in the number of variables, together with large interparameter correlation.

Atomic scattering factors used were taken from ref 8 and included corrections for anomalous dispersion for the niobium atom ($\Delta f' = -2.1$, $\Delta f'' = 0.9$). Crystallographic computer programs used in this determination have been cited elsewhere.[9] A table of the measured and calculated structure factors is available.[10]

The final atomic coordinates and thermal factors are listed in Table I. Table II gives the bond lengths and angles in the "NbO8" polyhedron, with parameters defining the shape of this polyhedron in Table III. Table IV shows the shortest interligand $O\cdots O$ contacts in some high-coordinate complexes. Bond lengths and angles in the tropolonato ligands are given in Table V, and least-squares mean planes associated with these ligands, in Table VI. A projection of the unit cell along the a axis is shown in Figure 1 and a diagram of the oxygen atom configuration is given in Figure 2.

Discussion

The "NbO8" Polyhedron. To describe the polyhedron formed by the eight oxygen donor atoms, we have used the criteria originally established by Porai-Koshits and Aslanov[11] and extended by Muetterties and Guggenberger.[12] The dihedral angles δ between pairs of faces which intersect along the "type b" edges of a dodecahedron are defined in order to distinguish polyhedra in the dodecahedral class. The "type b" edges are those which connect vertices at which five edges are joined (O_2, O_3, O_5, and O_8 in this case). Also defined is the angle (φ), which represents the twist that occurs in the diagonal trapezoids of a regular dodecahedron as a result of distortion. The values of φ for the trapezoids defined by

Table I

a. Fractional Atomic Coordinates ($\times 10$) in Crystalline $(NbT_4)_2(O(H\cdots Cl)_3)\cdot CH_3CN^a$

Atom type	Coordinates			Atom type	Coordinates		
	x	y	z		x	y	z
Nb	4544 (1)	2816 (1)	1013 (1)	$3C_4$	1009 (12)	1194 (15)	1286 (8)
Cl_1	0	418 (6)	2500	$3C_5$	1627 (12)	1148 (14)	1725 (7)
Cl_2	220 (4)	3546 (5)	1621 (2)	$3C_6$	2498 (12)	1415 (14)	1766 (7)
O_1	5147 (6)	2958 (8)	1768 (4)	$3C_7$	2971 (12)	1849 (12)	1401 (7)
O_2	5790 (7)	3390 (8)	955 (4)	$4C_1$	3982 (10)	4656 (13)	590 (6)
O_3	5201 (7)	1505 (8)	1109 (4)	$4C_2$	3863 (11)	5473 (13)	225 (6)
O_4	4836 (6)	2307 (9)	297 (4)	$4C_3$	3524 (12)	6412 (15)	285 (7)
O_5	3296 (7)	2482 (8)	628 (4)	$4C_4$	3207 (13)	6774 (16)	710 (9)
O_6	3800 (7)	2083 (9)	1525 (4)	$4C_5$	3177 (13)	6416 (16)	1198 (8)
O_7	4338 (7)	3949 (9)	474 (4)	$4C_6$	3385 (11)	5512 (14)	1368 (7)
O_8	3897 (7)	3944 (9)	472 (4)	$4C_7$	3755 (10)	4760 (12)	1108 (6)
O_9	360 (14)	2415 (19)	2555 (11)	$1H_2$	7301	4030	985
N	3403 (20)	898 (22)	2952 (11)	$1H_3$	8453	4106	1607
C_1	5000	729 (26)	2500	$1H_4$	8464	3928	2455
C_2	4042 (28)	809 (31)	2794 (16)	$1H_5$	7354	3623	2897
$1C_1$	5951 (11)	3249 (12)	1835 (7)	$1H_6$	5964	3190	2623
$1C_2$	6341 (11)	3340 (13)	2357 (7)	$2H_2$	6190	97	1197
$1C_3$	7220 (11)	3601 (14)	2525 (7)	$2H_3$	6828	-814	647
$1C_4$	7903 (12)	3836 (14)	2254 (7)	$2H_4$	6873	-608	-210
$1C_5$	7894 (11)	3943 (14)	1725 (7)	$2H_5$	6183	417	-703
$1C_6$	7184 (12)	3846 (13)	1325 (7)	$2H_6$	5327	1612	-548
$1C_7$	6344 (10)	3501 (12)	1392 (6)	$3H_2$	1739	2166	275
$2C_1$	5564 (12)	1100 (14)	721 (7)	$3H_3$	601	1487	575
$2C_2$	6091 (12)	287 (14)	835 (7)	$3H_4$	433	948	1331
$2C_3$	6501 (13)	-268 (16)	487 (8)	$3H_5$	1420	880	2036
$2C_4$	6512 (13)	-159 (16)	-37 (8)	$3H_6$	2820	1322	2095
$2C_5$	6094 (13)	498 (15)	-342 (8)	$4H_2$	4030	5320	-112
$2C_6$	5557 (11)	1252 (13)	-248 (7)	$4H_3$	3547	6819	-16
$2C_7$	5311 (11)	1563 (14)	251 (7)	$4H_4$	2958	7414	647
$3C_1$	2691 (10)	2115 (14)	877 (6)	$4H_5$	2956	6842	1450
$3C_2$	1843 (11)	1954 (13)	623 (7)	$4H_6$	3302	5387	1718
$3C_3$	1114 (12)	1537 (14)	813 (7)				

b. Thermal Motion Parameters ($\times 10^3$ A^2) in Crystalline $(NbT_4)_2(O(H\cdots Cl)_3)\cdot CH_3CN$

Anisotropic Atoms^b

Atom type	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Nb	30 (1)	35 (1)	19 (1)	-1 (1)	-6 (1)	1 (1)
Cl_1	64 (5)	59 (6)	66 (6)	0	23 (4)	0
Cl_2	99 (5)	81 (5)	63 (4)	10 (4)	6 (4)	13 (4)
O_1	18 (6)	53 (9)	28 (6)	-12 (6)	-4 (5)	-8 (6)
O_2	30 (7)	57 (9)	27 (7)	-4 (6)	-12 (6)	11 (6)
O_3	53 (8)	37 (8)	31 (8)	19 (7)	-4 (6)	12 (6)
O_4	38 (6)	48 (6)	16 (6)	9 (6)	11 (5)	-5 (6)
O_5	30 (7)	51 (10)	31 (7)	-5 (6)	-7 (5)	4 (6)
O_6	31 (6)	49 (9)	27 (6)	-6 (7)	-2 (6)	9 (7)
O_7	35 (7)	54 (9)	20 (6)	2 (6)	3 (5)	2 (6)
O_8	58 (8)	49 (9)	35 (8)	6 (7)	-3 (7)	9 (7)

Isotropic Atoms

Atom type	U	Atom type	U	Atom type	U
O_9	69 (9)	$2C_1$	42 (5)	$3C_5$	48 (5)
C_1	88 (11)	$2C_2$	44 (5)	$3C_6$	51 (6)
C_2	59 (12)	$2C_3$	61 (6)	$3C_7$	39 (5)
N	45 (9)	$2C_4$	61 (6)	$4C_1$	26 (4)
$1C_1$	32 (5)	$2C_5$	59 (6)	$4C_2$	35 (5)
$1C_2$	34 (5)	$2C_6$	41 (5)	$4C_3$	51 (6)
$1C_3$	42 (5)	$2C_7$	35 (5)	$4C_4$	61 (6)
$1C_4$	45 (5)	$3C_1$	32 (4)	$4C_5$	58 (6)
$1C_5$	45 (5)	$3C_2$	41 (5)	$4C_6$	43 (5)
$1C_6$	46 (5)	$3C_3$	45 (5)	$4C_7$	28 (4)
$1C_7$	28 (4)	$3C_4$	56 (6)		

^{a} The least-squares estimated errors are in parentheses. ^{b} Expressed in the form $\exp[-2\pi^2(ha^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$.

$(O_1O_6O_5O_2)$ and $(O_3O_4O_7O_8)$ are listed with the values of δ for the NbT_4^+ cation and the ScT_4^- anion[1] in Table III, alongside the corresponding values of δ and φ for regular polyhedra in this class. From these results, the polyhedron formed by the eight oxygen donor atoms in the NbT_4^+ cation is best described (as in the case of $(HScT_4)_2^1$) as an irregular bicapped trigonal prism, distorted toward a dodecahedron.

Contributions to the energy of eight-coordinate polyhedra have been listed by Hoard and Silverton[2] as (1) direct interaction of the central atom with its ligands, (2) mutual repulsions of the ligands, (3) the effect of nonbonding electrons in the valence shell of the central atom, and (4) constraints imposed by multidentate ligands. Direct bonding interaction is considered to be essentially equivalent for the dodecahedral and square-antiprismatic polyhedra,[2] and nonbonding electron repulsions do not occur in the Nb(V) metal ion studied here. The effect of factors 2 and 4 on the eight-coordinate stereochemistry of M(biden)₄ systems has been studied by Blight and Kepert.[3] They have shown that, neglecting any interactions between ligands save that of interligand repulsion, the

potential energy surfaces produced in an M(biden)₄ system are dependent on two parameters: a repulsive exponent term n and a term b which is the ratio of the donor atom separation to the metal to donor atom bond length. The dimensions of a generalized eight-coordinate stereochemistry which is calculated[3] to have the most stable configuration for values of $b = 1.10$ and 1.15 are listed in Table IIIb, alongside the parameters determined for the "NbO₈" ($b = 1.16$) and "ScO₈" ($b = 1.13$) polyhedra. The agreement between these sets of parameters is seen to be quite close. Bond lengths and angles within the "NbO₈" polyhedron are given in Table II, and a perspective view of the "NbO₈" polyhedron is shown in Figure 2.

As stated earlier, it was assumed on the basis of previous structural studies,[1,4,5] that the O$\cdots$O "bite" in the tropolonato ligand would be a constant in the calculation of b for a series of tetrakis(tropolonates). The results shown in Table II show that this assumption is not correct: the average ligand bite is 2.43 (2) Å which is significantly less than the previously determined shortest value of 2.490 (6) Å,[4] and thus the value

Table II. Interatomic Distances and Angles in the "NbO$_8$" Polyhedron, the (O(H···Cl)$_3$)$^{2-}$ Anion, and the CH$_3$CN Molecule

Distances, A

Nb-O$_1$	2.088 (9)	O$_2$-O$_7$	2.547 (14)
Nb-O$_2$	2.070 (11)	O$_2$-O$_8$	3.226 (18)
Nb-O$_3$	2.084 (11)	O$_3$-O$_5$	3.325 (14)
Nb-O$_4$	2.070 (10)	O$_3$-O$_6$	2.600 (16)
Nb-O$_5$	2.104 (9)	O$_4$-O$_5$	2.574 (15)
Nb-O$_6$	2.070 (10)	O$_4$-O$_7$	2.467 (17)
Nb-O$_7$	2.111 (11)	O$_5$-O$_7$	2.637 (16)
Nb-O$_8$	2.092 (13)	O$_5$-O$_8$	2.860 (16)
O$_1$-O$_2$	2.476 (16)	O$_6$-O$_8$	2.652 (18)
O$_3$-O$_4$	2.398 (14)	O$_9$-Cl$_1$	2.84 (3)
O$_5$-O$_6$	2.438 (14)	O$_9$-Cl$_2$	2.88 (2)
O$_7$-O$_8$	2.417 (17)	Cl$_1$-Cl$_2$	4.94 (1)
O$_1$-O$_3$	2.654 (17)	Cl$_2$-Cl$_2$'	4.67 (1)
O$_1$-O$_6$	2.410 (14)	O$_9$-O$_9$	1.11 (2)
O$_1$-O$_6$	2.508 (15)	C$_1$-C$_2$	1.71 (5)
O$_2$-O$_3$	2.815 (17)	C$_1$-N	2.80 (3)
O$_2$-O$_4$	2.608 (14)	C$_2$-N	1.09 (5)

Angles, Deg

O$_1$NbO$_2$	73.1 (0.4)	O$_3$NbO$_5$	105.1 (0.4)
O$_3$NbO$_4$	70.5 (0.5)	O$_3$NbO$_6$	77.1 (0.5)
O$_5$NbO$_6$	71.1 (0.4)	O$_4$NbO$_5$	76.1 (0.4)
O$_7$NbO$_8$	70.2 (0.5)	O$_4$NbO$_7$	72.3 (0.5)
O$_1$NbO$_3$	79.0 (0.4)	O$_5$NbO$_7$	77.5 (0.4)
O$_1$NbO$_6$	70.5 (0.4)	O$_5$NbO$_8$	86.0 (0.4)
O$_1$NbO$_8$	73.7 (0.4)	O$_6$NbO$_8$	78.8 (0.5)
O$_2$NbO$_3$	85.3 (0.5)	Cl$_1$O$_9$Cl$_2$	119.8 (0.9)
O$_2$NbO$_4$	78.1 (0.4)	Cl$_2$O$_9$Cl$_2$'	108.7 (0.9)
O$_2$NbO$_7$	75.1 (0.4)	C$_1$NC$_2$	174 (4)
O$_2$NbO$_8$	101.6 (0.5)		

Table III

a. Values of δ and φ^a for Regular Polyhedra of the Dodecahedral Class, for HScT$_4$,[1] and for NbT$_4^+$

	δ, deg				φ, deg	
Dodecahedron	29.5	29.5	29.5	29.5	0	0
Bicapped trigonal prism	0	21.7	48.2	48.2	14.1	14.1
Square antiprism	0	0	52.5	52.5	24.5	24.5
HScT$_4$	13.4	29.0	43.0	42.5	10.8	10.8
NbT$_4^+$	19.4	21.0	42.9	45.1	11.5	13.9

b. Angular Parameters (deg) for M(biden)$_4$ of Intermediate Geometry^b and for the "ScO$_8$" and "NbO$_8$" Polyhedra

	Predicted values		HScT$_4$	NbT$_4^+$
	b = 1.10	b = 1.15	b = 1.13	b = 1.16
φ$_A$	37.4	34.4	37.8	37.8
ψ$_A$	50.9	51.2	55.0	54.3
φ$_B$	50.6	53.7	48.3	49.7
ψ$_B$	14.8	16.9	15.5	16.3

^{a} As defined in ref 10. ^{b} From ref 3.

of b = 1.16 is not substantially different from that for (HScT4)2 (b = 1.13), and no large difference in geometry is predicted.

The most striking feature of the "NbO8" polyhedron is the wide range of interligand O···O distances (Table II). In the regular dodecahedron, the ratio of the length of the "type b" edges to the other edges (all of which are equivalent) is 1.25; in the "NbO8" polyhedron, this ratio (based on the interligand distances) averages 1.20 but varies from 1.1 to 1.4. In particular, the O1-O6 (2.410 (14) Å) and O4-O7 (2.467 (17) Å) edges are short compared to other interligand compounds of the same type (which vary from 2.508 (15) to 2.654 (17) Å and average 2.60 Å). Such results cannot be rationalized on the basis of interligand repulsion alone. These short edges connect tropolonato ligands which are arranged in such a way that the lone pairs of electrons on each of the sp^2 hybridized oxygen atoms involved in the contact overlap in the space between the nuclei of oxygen atoms. The niobium complex

Table IV. Shortest Interligand O···O Contacts in Some High-Coordinate Complexes, the Bidentate Ligand "Bites" in Each Complex, and the Mean M-O Distance for These Ligands

Complex	Shortest interligand contacts, A	Ligand "bite", A	Mean M-O, A	Ref
NbT$_4^+$	2.41	2.48	2.08	Table
	2.47	2.44		II
		2.42		
		2.40		
ScT$_4^-$	2.57	2.52	2.21	1
	2.70	2.50		
		2.50		
		2.50		
ThT$_4$·DMF	2.80	2.56	2.45	15
		2.53		
		2.55		
		2.52		
W(C$_9$H$_5$NOBr)$_4$	2.33	2.53^a	2.07	14
	2.33	2.51^a		
		2.48^a	2.20^b	
		2.48^a		
T$_3$SnOH	2.52	2.54	2.16	16
	2.57	2.54		
	2.51	2.60		
T$_3$SnCl	2.53	2.59	2.13	16
	2.52	2.54		
	2.52	2.55		
Zr(ox)$_4$	2.63	2.55	2.20	17
	2.51	2.58		
Ti(NO$_3$)$_4$	2.51	2.14	2.07	18
	2.51	2.13		
		2.13		
		2.12		
Sn(NO$_3$)$_4$	2.72	2.13	2.16	19
	2.75	2.15		
		2.14		
		2.13		
Fe(NO$_3$)$_4^-$	2.68	2.13	2.14	20
Zr(MeCOCH-COMe)$_3$Cl	2.46	2.68	2.12	21
	2.53	2.68		
	2.56	2.68		
Sb(C$_2$O$_4$)$_3$E^c	2.59	2.62	2.26	22
	2.71	2.62		
	2.71			

^{a} O···N bite. ^{b} M-N distance. ^{c} E = lone pair.

reported here appears to be an extreme example of a correlation between short interligand O···O distances, and the overlap of lone pairs on adjacent oxygen atoms. Table IV gives a list of the shortest interligand contacts in some high-coordinate complexes[14-22] containing bidentate ligands with oxygen donor atoms. In each case the geometry involved in these contacts would allow overlap of the lone pairs of the oxygen atoms involved in the short nonimposed contact. Lone pair interactions which may be attractive in nature have been proposed for molecules of appropriate symmetry.[23] Another, possibly essential, unifying feature of these complexes is the presence of empty valence-shell d orbitals. However, it should be noted that the two short contacts are between pairs of oxygen atoms related by an approximate $\bar{4}$ axis (assuming approximate D$_{2d}$ symmetry for the polyhedron); the lowest energy unoccupied orbital for this arrangement[13] is d$_{xy}$ and not d$_{z^2}$ which would be required for interaction with the lone pairs.

It is tentatively suggested that, for the short contacts listed in Table IV, conditions exist in the arrangement of the lone pairs (and in the presence of empty metal d orbitals), for interactions to occur which would oppose the coulombic re-

Table V. Dimensions within the Tropolonato Ligands

a. Bond Lengths, with Mean Values ($\bar{l}$), of Chemically Equivalent Bonds, together with $\sigma_{\bar{l}}$ and σ_s,[a] and the Mean Values of the Same bonds Calculated from Previously Determined Structures[1,4,5] (Å)

Bond type	Ligand type 1	2	3	4	$\bar{l}$ ($\sigma_{\bar{l}}$)	σ_s[b]	Previous mean value
C_1-O_1	1.281 (17)	1.317 (21)	1.277 (18)	1.296 (18)	1.300 (9)	0.025	1.287 (2)
C_2-O_7	1.351 (16)	1.275 (19)	1.309 (18)	1.294 (18)			
C_1-C_7	1.387 (22)	1.397 (23)	1.431 (22)	1.415 (41)	1.408 (10)	0.020	1.462 (6)
C_1-C_2	1.427 (21)	1.401 (23)	1.406 (20)	1.374 (21)	1.402 (9)	0.024	1.405 (4)
C_6-C_7	1.390 (22)	1.445 (23)	1.379 (25)	1.392 (22)			
C_2-C_3	1.411 (21)	1.377 (26)	1.406 (20)	1.419 (25)	1.392 (9)	0.027	1.384 (2)
C_5-C_6	1.427 (22)	1.366 (25)	1.367 (23)	1.362 (25)			
C_3-C_4	1.344 (24)	1.369 (26)	1.337 (24)	1.342 (26)	1.358 (9)	0.025	1.380
C_4-C_5	1.377 (29)	1.329 (25)	1.404 (23)	1.364 (27)			

(b) Bond Angles (deg)

Angle type	Ligand type 1	2	3	4
$C_7C_1C_2$	126.1 (1.6)	131.2 (1.9)	125.2 (1.7)	128.3 (1.7)
$C_1C_2C_3$	127.5 (1.7)	126.9 (1.8)	129.0 (1.6)	128.5 (1.8)
$C_2C_3C_4$	130.9 (1.6)	129.3 (2.0)	130.2 (1.7)	126.8 (2.0)
$C_3C_4C_5$	127.6 (1.6)	127.9 (2.2)	128.9 (1.9)	131.8 (2.1)
$C_4C_5C_6$	130.1 (1.8)	133.1 (2.1)	128.1 (2.0)	127.8 (2.1)
$C_5C_6C_7$	125.5 (1.8)	126.7 (1.7)	128.8 (1.8)	129.3 (1.8)
$C_6C_7C_1$	131.4 (1.5)	124.6 (1.8)	129.6 (1.6)	127.2 (1.6)
$O_1C_1C_7$	116.5 (1.4)	111.4 (1.3)	114.8 (1.3)	111.5 (1.5)
$O_2C_7C_2$	112.4 (1.4)	113.9 (1.7)	111.0 (1.5)	113.9 (1.5)
$O_1C_1C_2$	117.3 (1.6)	117.3 (1.7)	119.9 (1.4)	120.1 (1.6)
$O_2C_7C_6$	116.1 (1.5)	121.5 (1.5)	119.4 (1.6)	118.8 (1.6)
NbO_1C_1	118.9 (0.9)	121.0 (0.8)	120.4 (0.8)	122.4 (0.8)
NbO_2C_7	118.9 (0.8)	122.2 (0.8)	122.0 (0.8)	121.7 (0.8)

[a] As defined in the text. [b] These values can be compared to the least-squares errors given in parentheses after each bond length (see text).

**Table VI.** Atomic Displacements from the Least-Squares Planes[a] Relevant to the Discussion of Structure in $(NbT_4)_2(O(H\cdots Cl)_3)\cdot CH_3CN$

Plane	Equation of the LS plane	χ^2 [b]
P	$0.296X - 0.952Y - 0.072Z + 2.163$	30.1
Q	$-0.799X - 0.586Y - 0.131Z + 7.740$	2.4
R	$0.313X - 0.901Y - 0.299Z + 2.108$	4.1
S	$-0.894X - 0.336Y - 0.298Z + 7.93$	6.5

Displacements, Å

Ligand 1 Plane P		Ligand 2 Plane Q		Ligand 3 Plane R		Ligand 4 Plane S	
O_1	0.016	O_3	0.049	O_5	0.021	O_7	-0.056
O_2	0.016	O_4	-0.049	O_6	0.001	O_8	0.057
$1C_1$	0.048	$2C_1$	-0.005	$3C_1$	-0.015	$4C_1$	0.008
$1C_2$	-0.033	$2C_2$	0.005	$3C_2$	-0.001	$4C_2$	0.014
$1C_3$	-0.027	$2C_3$	0.012	$3C_3$	0.012	$4C_3$	0.017
$1C_4$	0.037	$2C_4$	-0.017	$3C_4$	-0.003	$4C_4$	0.0214
$1C_5$	0.027	$2C_5$	-0.004	$3C_5$	-0.023	$4C_5$	-0.005
$1C_6$	-0.060	$2C_6$	0.017	$3C_6$	0.020	$4C_6$	0.008
$1C_7$	0.005	$2C_7$	-0.010	$3C_7$	0.008	$4C_7$	-0.015
Nb	0.218	Nb	-0.212	Nb	-0.131	Nb	-0.099

[a] The orthogonal system of axes (X, Y, Z) has X along the a axis, Y in the ab plane, and Z along the c^* axis. The weights used in the calculation of LS planes are given by $W_i = W_{i,1}/\sigma^2 = 3/[\sigma^2(X_i) + \sigma^2(Y_i) + \sigma^2(Z_i1)]$. [b] χ^2 for a plane $lM + mY + nZ - p = 0$ for N atoms is given by $\Sigma_{i=1}^{i=N}(P_i^2/\sigma^2(P_i))$, where $\sigma^2(P_i) = l^2\sigma^2(X_i) + m^2\sigma^2(Y_i) + n^2\sigma^2(Z_i)$ and P_i is the distance of atom i from the plane.

pulsive force, thus stabilizing the short contact. Such an interaction, the possibility of which has been briefly mentioned in a previous eight-coordinate structural determination,[14] would need to be included in any theory of those high-coordinate geometries where these arrangements of lone pairs occur. In all the cases listed in Table IV, oxygen donor atoms and metal atoms involved in the contact are approximately planar. (The lone pairs can be assumed to be approximately coplanar since the C–O bond has significant π character.)
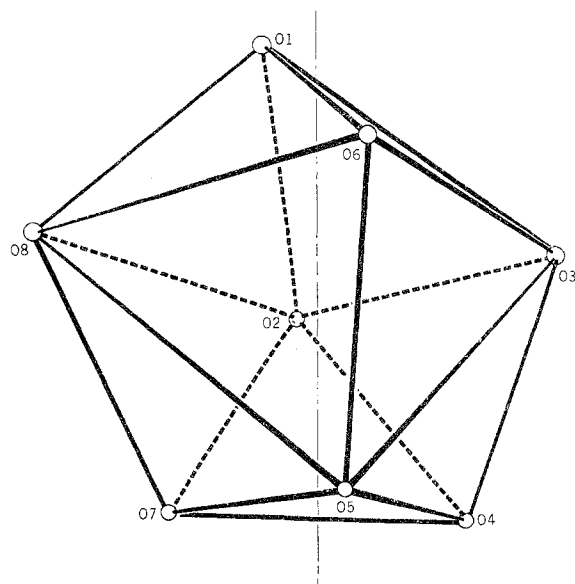
Figure 2. Perspective view of the irregular bicapped trigonal prism as observed in the NbT_4^+ cation. The distortion toward a dodecahedron is illustrated by the vertical broken line which indicates the direction of the approximate $\bar{4}$ axis.

In the approximately pentagonal-bipyramidal structures of the type $M(biden)_3X$ listed in Table IV,[16,21,22] two short interligand contacts also occur between the two bidentate ligands that lie in the approximate pentagonal plane and the other bidentate ligand which is nearly perpendicular to this plane. However, the lone pairs of electrons on the three oxygen atoms involved in these two contacts can still be envisaged as overlapping, and a similar decrease in the repulsion forces is suggested.

Frequently the systems which involve oxygen polyhedra around metal atoms are considered as moving to an

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"electrostatic minimum energy configuration". If this is the case one might expect to get relatively little variation in the nonimposed short contacts but this is *not* the case as can be seen from the data presented.

The Tropolonato Ligands. Bond lengths and angles for the tropolonato ligands in this complex are given in Table V. Shown also in Table V are the mean values $\bar{l}$ of the bonds within the four ligands which are considered to be chemically equivalent and σ_s (the error based on the internal consistency of the structure, as defined earlier in the text). The corresponding values of $\bar{l}$ for all previously determined tropolonato complexes[1,4,5] are also listed, and, except in the case of the C_1-C_7 bond length, the mean values in the NbT$_4^+$ cation are, within the error expressed by $\sigma\bar{l}$, equal to the general mean values. Examination of the structural data available on tropolonato ligands[1,4,5] reveals that increasing strength of the complexing bonds is accompanied by lengthening of the C–O bonds and also some shortening of the C_1-C_7 bonds. The values of the C_1-C_7 bonds (Table V) do not differ significantly from values obtained for strongly complexing tropolonato ligands (e.g., 1.439 (15) Å in T$_3$SnCl).[16]

Three of the C$_7$ rings in the ligands are planar (relevant least-squares mean planes are given in Table VI), and in the fourth, the distortions are not chemically significant. Deviations of the corresponding oxygen atoms from these planes are small (0.001–0.057 Å), though larger deviations of the niobium atom from each plane (0.099–0.218 Å) are observed.

The (O(H···Cl)$_3$)$^{2-}$ Anion. The arrangement of a flattened pyramidal hydroxonium ion (H$_3$O$^+$), triply bonded to three chlorine atoms at the vertices of the base of the pyramid (O···Cl = 2.87 (3) Å), has been found previously in the structures of hydrogen chloride monohydrate[24] (O···Cl = 2.95 (1) Å) and cesium chloride–0.33(hydroxonium bichloride) (O···Cl = 2.92 (2) Å).[25] It is interesting to note that the same type of disorder is proposed in all three structures, with equal probability that the oxygen will be above or below the plane formed by the three chlorine atoms. No evidence for the hydrogen atom positions in this anion was found from the data, which is not surprising in view of the occupancy numbers of 0.25 or 0.5 which would be assigned to them. Bond lengths and angles

for this anion and for the acetonitrile molecules of crystallization are included in Table II.

Registry No. (NbT$_4$)$_2$(O(H···Cl)$_3$)·CH$_3$CN, 56630-15-0.

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 Business Office, Books and Journals Division, 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 AIC503069-12-75.

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Coordination of Perrhenate Ion in a Five-Coordinate Square-Pyramidal Copper(II) Complex. Crystal Structure of Perrhenato-2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II)

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The crystal structure of perrhenato-2,2'-(1,3-diaminopropane)bis(2-methyl-3-butanone oximato)copper(II), [Cu-(PnAO-H)(ReO$_4$)], has been determined from three-dimensional X-ray data collected with a scintillation counter. The orthorhombic unit cell dimensions are a = 11.989 (6), b = 12.430 (6), and c = 13.258 (7) Å. The density of 1.968 (2) g/cm^3 calculated for four molecules per unit cell agrees with the flotation density of 1.96 (2) g/cm^3. The space group is *Pmcn*. A full-matrix least-squares refinement gave a final conventional agreement factor of 5.2%. The structure consists of discrete five-coordinate square-pyramidal copper(II) neutral complexes. The tetradentate α-amine oxime ligand is bonded in a square plane about the copper with Cu–N(amine) = 1.99 (1) Å and Cu–N(oxime) = 1.96 (1) Å. The apical position of the square pyramid is occupied by a perrhenate oxygen (Cu–O = 2.40 (1) Å and Re–O(av) = 1.70 (3) Å). The copper atom is significantly (0.24 Å) out of the plane of the four nitrogens toward the perrhenate ion. The short intramolecular hydrogen bond involves a separation of oxime oxygens of 2.46 (2) Å.

Introduction

A comprehensive study of the short intramolecular hydrogen bonds in α-amine oxime complexes of metal ions is in progress in order to examine the effect of the O---O distance on the hydrogen atom position and the associated potential function.

Previous structural studies have involved a bidentate α-amine oxime with Ni(II),[1,2] Pt(II),[3] and Co(III),[4] a tetradentate α-amine oxime (EnAO) with Ni(II),[5] and the present tetradentate α-amine oxime (PnAO) (Figure 1) with Co(III).[6] Changing steric requirements of the ligand and changing the