

On the monocrystal, rutile has a sharp texture of topotactic type, with the (110) plane remaining nevertheless parallel to the monocrystal face.

The macroscopic geometry of the metal seems to play as important a part as its crystal orientations.

Results are given in the table below. The values obtained from (I) and (II) agree to within 3σ in all but three cases. More interesting, but not surprising, the standard distances to oxygen obtained here mainly from organic molecular compounds with mixed coordinative environments agree with those obtained by Brown and Shannon from oxides and inorganic oxyacid salts.

Table: Standard bond lengths d_{iO} ($CN_O = 4$); values for other CN's may be obtained from (I), (II), c and N.

	Mg	Al	Si	P	
C		2.032(3)	1.872(1)	1.788(1)	a)
		2.032(3)	1.872(1)	1.786(1)	b)
N		1.851(10)	1.721(5)	1.616(1)	a)
		1.850(9)	1.718(4)	1.615(1)	b)
O	1.885(14)	1.701(7)	1.610(4)	1.534(1)	a)
	1.898(11)	1.715(6)	1.613(4)	1.534(1)	b)
F			1.500(6)	1.402(3)	a)
			1.520(5)	1.418(3)	b)
Si(-Si)			2.391(11)	2.168(22)	a)
P(-P)			2.391(15)	2.145(26)	b)
Cl	2.297(17)	2.131(3)	2.026(8)	1.935(5)	a)
	2.281(17)	2.131(3)	2.022(8)	1.913(5)	b)
c	0.501(37)	0.466(19)	0.455(13)	0.484(6)	a)
N	4.31(30)	4.25(16)	4.01(11)	3.41(4)	b)
σ^2	0.0858	0.0195	0.0099	0.0067	a) c)
	0.0785	0.0182	0.0099	0.0065	b) c)
m	504	522	826	1878	c)
N _{obs}	89	117	189	441	c)

a) (I); b) (II); c) m=number of distances used in refinement; N_{obs}=number of structures in data set; p=number of standard bond lengths refined $\sigma^2 = (\sum N_{obs} - \sum N_{calc})^2 / N_{obs} - (p + 1)$

04.1-7 STANDARD BOND LENGTHS IN MOLECULAR COMPOUNDS FROM EMPIRICAL BOND LENGTH-BOND STRENGTH RELATIONSHIPS (Mg,Al,Si,P-C,N,O,F,Cl) By G. Klebe, H.B. Bürgli, Laboratorium für Chemische und Mineralogische Kristallographie, Universität Bern, Freiestr. 3, CH-3012 Bern, Switzerland

Standard bond lengths are a prerequisite for interpretations and comparisons of interatomic distances. Such distances (d_O) are given here for bonds from Mg,Al,Si,P to C,N,O,F,Cl. They are based on least squares analysis using two empirical bond strength (n)-bond length(d) relationships: (I) $n_i/n_O = \exp[-(d_i/d_{iO})/c]$ (L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, (1940)); (II) $n_i/n_O = (d_i/d_{iO})^{-N}$ (G. Donnay and R. Allmann, Amer. Min. (1970), 55, 1003; I.D. Brown and R.D. Shannon, Acta Cryst. (1973), A29,266). The data for Al,Si,P with coordination numbers (CN) 4,5,6 were taken from the Cambridge Structural Data Base and supplemented with gas phase electron diffraction data; the data for Mg were taken from J.C.J. Bart and P. Vitarelli (Inorg. Chim. Acta (1983), 73, 215). The data include molecules with up to 4 different ligand atoms around the central atom. Details will be given in a future, full account of the work. Values of d_{iO} , c and N, respectively, were determined by minimizing the expression

$$(CN_O - \sum_{i=1}^{CN} n_i)^2$$

for Mg,Al,Si,P separately, but considering all coordination numbers simultaneously; CN_O is a reference coordination number, n_O is taken as 1.

04.1-8 CONTRIBUTION TO THE CRYSTAL CHEMISTRY OF SODIUM HEXACHLOROANTIMONATE, -NIOBATE, AND -TANTALATE. By Henning Henke, Institut für Anorg. Chemie der Universität Karlsruhe (TH), D 7500 Karlsruhe, Bundesrepublik Deutschland.

From single-crystal X-ray data collected at room temperature the individual structures of three sodium salts can be established:

	a [Å]	b [Å]	c [Å]	β [°]
NaSbCl ₆	6.393(2)	6.393	10.717(4)	--
NaNbCl ₆	6.398(2)	6.850(2)	19.012(4)	90.72(2)
NaTaCl ₆	6.449(2)	6.880(2)	18.989(6)	90.87(2)

While NaSbCl₆ is tetragonal with space group $P4_2/m$ and $Z=2$, the niobium and tantalum analogues crystallize both in the monoclinic space group $P2_1/c$; since there is a doubling of the c-axis the unit cell has $Z=4$. Parameter refinement includes absorption and extinction corrections; the final R-values are 0.018 (NaSbCl₆, 611 obs.refl.), 0.018 (NaNbCl₆, 2214 obs.refl.), and 0.024 (NaTaCl₆, 2341 obs.refl.). All three compounds contain discrete MCl₆⁻ ions arranged with their centres like PtCl₆²⁻ in cubic K₂PtCl₆. The same applies to the cations

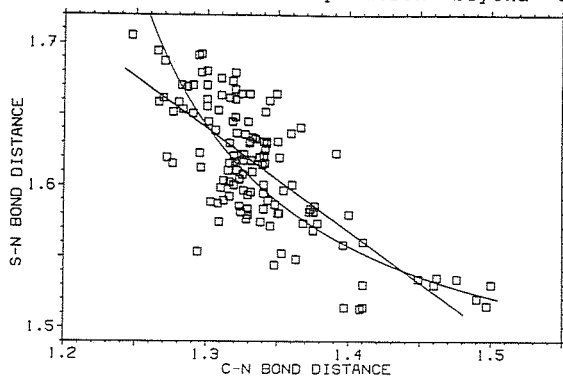
if half of the potassium positions are replaced by sodium, the rest will be looked at as voids \square . From this viewpoint $\text{Na}\square\text{NbCl}_6$ and the isotopic $\text{Na}\square\text{TaCl}_6$ represent low-symmetry variants of the K_2PtCl_6 structure. Among other features it is important to note that the sodium ions and voids occupy alternate layers aligned parallel to (001).

Despite similar unit-cell dimensions the structure of $\text{Na}\square\text{SbCl}_6$ differs in two respects. Sodium atoms and voids \square are found on separate rods which extend both in *c*-direction (Wyckoff positions 2e and 2f); the formation of separate layers $\parallel(001)$ is not observed. Another obstacle is the different orientation of the SbCl_6^- ions. A related arrangement is however shown by rutile where chains of interconnected TiO_6 units form a three-dimensional network. In the hexachloroantimonate two thirds of these 'octahedra' remain vacant to comply with stoichiometry, schematically $\square\square\text{SbCl}_6$. As in the case of rutile one obtains a threefold superstructure (space group $P4_2/mnm$, $c' = 3c$) with $P4_2/m$ being an immediate subgroup.

04.1-9 ON THE GEOMETRY AND THE BONDING RELATIONSHIPS AT THE TWOFOLD COORDINATED NITROGEN IN C-N-S AND S-N-S FRAGMENTS.
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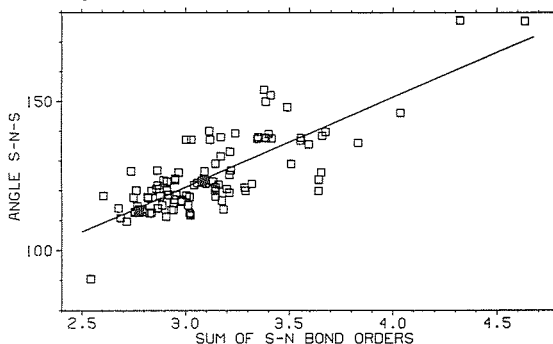
For molecular fragments C-N-S or S-N-S containing a twofold coordinated nitrogen, correlations can be found between the two bond distances and the enclosed bond angle derived from X-ray data. For both systems all coordination numbers of nitrogen bound atoms were permitted in these considerations.

The relationship between the two bond distances (SN vs. CN) in the C-N-S fragment is shown in Fig. 1. Due to the small variations of the bond angles, the latter may be in a first approximation neglected. The regression line is well defined by the 128 data points ($k = -0.75$) but is unsuitable for an extrapolation beyond the



given range of distances. For extrapolation a better description is provided by a hyperbolic function $d(\text{SN}) - d_1 = a / (d(\text{CN}) - d_2)$ ($k = 0.80$) which for very large values of the SN or CN distances leads to the known CN or SN triple bond lengths, respectively. Assuming that the sum in bond order of the two bonds to the nitrogen equals 3, the following relationships between bond order and bond distances can be deduced: $d(\text{SN}) - 1.3 = 0.45 / \text{BO}(\text{SN})$; $d(\text{CN}) - 1.0 = 0.48 / \text{BO}(\text{CN})$.

With respect to the S-N-S system, the correlation between the sum of bond orders (derived from the respective bond distances by the formula given above) and the enclosed bond angles is shown in Fig. 2. The least squares line shown has the form $\angle \text{SNS} / 30 = \text{BO}(\text{SN}) + \text{BO}(\text{SN}) + 1$ ($k = 0.80$). A comparable correlation between bond distances and angles has been previously proposed by Banister and Durrant (J. Chem. Res. (S) 1978, 150), who considered compounds with selected coordination numbers at the sulphur atoms.

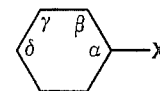


04.1-10 ANGULAR RING DISTORTIONS IN BENZENE DERIVATIVES: THE EFFECT OF THE NO_2 AND COOH SUBSTITUENTS

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Angular distortions in polysubstituted benzene rings may be described, at least as a first approximation, by superimposing separate contributions from each substituent. The effect of a substituent may then be expressed by a set of four 'angular substituent parameters', $\Delta\alpha = \alpha - 120^\circ$, $\Delta\beta = \beta - 120^\circ$, $\Delta\gamma = \gamma - 120^\circ$, $\Delta\delta = \delta - 120^\circ$.



Angular parameters for several substituents, including NO_2 and COOH , have been derived by regression from large samples of polysubstituted benzene rings [Domenicano & Murray-Rust, Tetrahedron Lett. 2283 (1979); Norrestam & Schepper, Acta Chem. Scand. A35, 91 (1981)]. We have recently shown, however, that deviations from additivity occur when a π -donor is para to a π -acceptor, due to cooperative interactions between substituents [Colapietro et al., Z. Naturforsch. 37b, 1309 (1982)]. There are also indications that deviations from additivity occur with some ortho-disubstituted derivatives. Accurate angular parameters must be derived, therefore, either by direct measurement on monosubstituted derivatives, or by regression from polysubstituted derivatives with appropriate patterns of substitution.

The following benzene derivatives, containing only NO_2