SHORT COMMUNICATIONS

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Acta Cryst. (1987). B**43**, 111

Structures cristallines à 415 K (phase II) et 295 K (phase III) de $KFeF_4$. Errata.

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Abstract

Owing to a typing error, $c = 13{\cdot}33$ Å was used instead of 12·33 Å in the bond-length and bond-angle calculations for phase III in the paper by Lapasset, Sciau, Moret & Gros [*Acta Cryst.* (1986), B**42**, 258-262]. The corrected data are given.

La dernière partie de la *Discussion, Géométrie des octaèdres,* doit être modifiée comme suit:

Les octaèdres FeF_6 paraissent réguliers et peu déformés (Tableau 2); leur géométrie est presque identique dans les deux phases étudiées. On observe des distances moyennes Fe-F terminaux nettement plus courtes (1,876 Å) que les distances Fe-F liés (1,967 Å). Ces valeurs sont semblables à celles obtenues dans NH_4FeF_4 (Leblanc, Ferey, De Pape & Teillet, 1985) où les distances correspondantes moyennes sont 1,867 et 1,956 Å.

Tableau 2. *Longueurs* (Å) *et angles* (°) *de liaisons*

Phase III			
Fe–F(1^{i})	1,954 (4)	K(2)–F(31^{vi})	2,646 (4)
Fe–F(1^{ii})	1,981 (4)	K(2)–F(31^{viii})	2,704 (3)
Fe–F(21)	1,968 (3)	K(2)–F(32^{v})	2,694 (4)
Fe–F(22^{iii})	1,970 (3)	F(1)–F(22^{ix})	2,794 (4)
Fe–F(31)	1,877 (3)	F(1)–F(22^{x})	2,764 (5)
Fe–F(32^{iii})	1,874 (3)	F(1)–F(21^{v})	2,798 (5)
K(1)–F(1)	3,226 (5)	F(1)–F(21^{i})	2,776 (4)
K(1)–F(21^{v})	3,905 (6)	F(1)–F(31^{i})	2,717 (5)
K(1)–F(21^{iv})	2,953 (6)	F(1)–F(31^{v})	2,704 (5)
K(1)–F(22^{vi})	3,840 (6)	F(1)–F(32^{vi})	2,700 (5)
K(1)–F(31^{v})	2,718 (4)	F(1)–F(32^{ix})	2,750 (5)
K(1)–F(32^{vi})	2,676 (4)	F(21)–F(31)	2,750 (4)
K(1)–F(32^{vii})	2,731 (3)	F(21)–F(32^{iii})	2,680 (4)
K(2)–F(1^{viii})	3,604 (5)	F(22)–F(31^{viii})	2,696 (4)
K(2)–F(21^{vi})	3,716 (5)	F(22)–F(32)	2,749 (4)
K(2)–F(22)	2,902 (6)	F(31)–F(32^{ix})	3,234 (5)
K(2)–F(22^{v})	3,720 (6)		
Fe^{i}–F(1)–Fe^{v}	166,0 (1)	F(1^{i})–Fe–F(31)	90,3 (2)
Fe–F(21)–Fe^{xi}	151,5 (2)	F(1^{ii})–Fe–F(31)	89,0 (2)
Fe^{viii}–F(22)–Fe^{xi}	152,3 (2)	F(1^{ii})–Fe–F(32^{iii})	91,0 (2)
F(1^{i})–Fe–F(1^{ii})	179,21 (3)	F(1^{i})–Fe–F(32^{iii})	89,7 (2)
F(31)–Fe–F(32^{iii})	179,8 (1)	F(21)–Fe–F(22^{iii})	179,6 (2)
F(1^{i})–Fe–F(21)	90,1 (1)	F(21)–Fe–F(31)	91,3 (2)
F(1^{ii})–Fe–F(21)	90,3 (1)	F(21)–Fe–F(32^{iii})	88,4 (2)
F(1^{i})–Fe–F(22^{iii})	89,6 (1)	F(22^{iii})–Fe–F(31)	89,0 (2)
F(1^{ii})–Fe–F(22^{iii})	90,0 (1)	F(22^{iii})–Fe–F(32^{iii})	91,3 (2)

Codes de symétrie: (i) $-x, -y, 1-z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $x-1, y, z$; (iv) $x, y, z+1$; (v) $x, \frac{1}{2}-y, z+\frac{1}{2}$; (vi) $1-x, -y, 1-z$; (vii) $x-1, y, 1+z$; (viii) $1+x, y, z$; (ix) $x-1, \frac{1}{2}-y, z+\frac{1}{2}$; (x) $x-\frac{1}{2}, -y, 1-z$; (xi) $\frac{1}{2}-x, y, z$; (xii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xiii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xiv) $\frac{3}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$; (xv) $x, y, z-1$; (xvi) $\frac{1}{2}-x, \frac{1}{2}-y, z-\frac{1}{2}$.

Références

Lapasset, J., Sciau, P., Moret, J. & Gros, N. (1986). *Acta Cryst.* B**42**, 258-262.

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Bond-length–bond-strength correlation between N–O and C–N of pyridine *N*-oxides.

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Abstract

An empirical correlation is established between N–O and C–N bond lengths of pyridine 1-oxides involved in both hydrogen bonding and metal complexes, leading to a decrease of N–O π-bond order from 35% in the free *N*-oxide to about 14% in its metal complexes.

Pyridine 1-oxide (PyO) is known to form hydrogen-bonded adducts with strong acids (H*A*), normally 1:1 adducts PyO.H*A*, sometimes also 2:1 adducts $(PyO\cdots H\cdots OPy)^+A^-$ (Hadzi, 1962). Hydrogen bonding has a pronounced effect on both the N–O and C–N bonds of the *N*-oxide. Seventy-

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eight crystal structures containing pyridine *N*-oxides were retrieved from the Cambridge Structural Database (Allen *et al.*, 1979). From these data, compiled in Table 1,* it is obvious that N–O bonds involved in hydrogen bonding are lengthened with respect to the free N–O function - the shorter the bridge, the longer N–O, whereas C–N approaches the value in pyridine, which is 1·3376 (4) Å (Sørensen, Mahler & Rastrup-Andersen, 1974). This effect is not restricted to hydrogen bonding, it is also observed in metal complexes of pyridine *N*-oxides. A plot of C–N *versus* N–O (Fig. 1) for the data of Table 1 shows a definite correlation. This correlation plot does not apply, however, to *ortho*-substituted pyridine *N*-oxides when *p* electrons of the substituent enter into conjugation with the aromatic π system. (In this case the C–N distance of the corresponding pyridine compound already deviates from its standard value of 1·337 Å.)

To get to a more quantitative description we start from Pauling's (1962) relation $d(n) = d(1) - c \log(n)$ for the dependence of the bond length d on the bond number n, $d(1)$ being the bond length for $n = 1$, *i.e.* the single-bond length. Taking the distance of 1·405 (5) Å in gaseous nitric acid (Millen & Morton, 1960) for an N–O single bond, and the N–O length of 1·250 (9) Å in the nitrite ion of $Ba(NO_2)_2.H_2O$ (Schäfer & Fischer, 1981) for a bond number $n = 1·5$, we find a constant $c = 0·88$ for the N–O bond. This yields a bond length of 1·14 Å for $n = 2$ in agreement with Allmann's (1975) value for the N=O double bond between sp^2-hybridized atoms. The mean length of 1·293 Å of the free NO function corresponds to $n = 1·34$, *i.e.* about one-third double-bond character. This is reduced to about 14% in strongly hydrogen-bonded *N*-oxides.

Similarly, we get $c = 0·53$ for the C–N bond using Allmann's (1975) values for a C–N single and double bond (1·43 and 1·27 Å respectively, for sp^2 hybrids). From this we calculate 1·337 Å for $n = 1·5$, in accord with the C–N length in pyridine and its derivatives.

If we make the assumption that the O is simply added to the N atom when going from pyridine to its *N*-oxide, the sum of bond numbers around the N atom amounts to $n(\text{C–N}) + n(\text{C–N}) + n(\text{N–O}) = 1·5 + 1·5 + 1 = 4$. Presuming a constant sum of bond numbers under all possible geometries, we have

$$d(\text{N–O}) = 1·405 - 0·88 \log[n(\text{N–O})] \quad (\text{Å}), \qquad (1)$$

$$d(\text{C–N}) = 1·430 - 0·53 \log\{[4 - n(\text{N–O})]/2\} \quad (\text{Å}). \qquad (2)$$

These equations describe the actual dependence very well (broken line in Fig. 1). Apparently, they are equally valid for pyridine *N*-oxides involved in hydrogen bonding as well as for their metal complexes. Both a proton H^+ and a cation Me^{n+} interacting with the lone pairs at the O atom tend to diminish the resonance between the O-atom's lone pairs and the aromatic system of the pyridine ring. This increased localization of the O atom's *p* electrons results in a decrease of the π-bond order of N–O and in a subsequent lengthening of that bond. The observed constancy of bond numbers may be interpreted as an approximate invariance of the sum of bond energies: the energy required to stretch the N–O bond is compensated by a comparable amount of energy gain from a shortening of the C–N bonds. Thus, Fig. 1 may be expected to describe not only a path of bond-number conservation but also a path of minimal energy change (Bürgi, 1975).

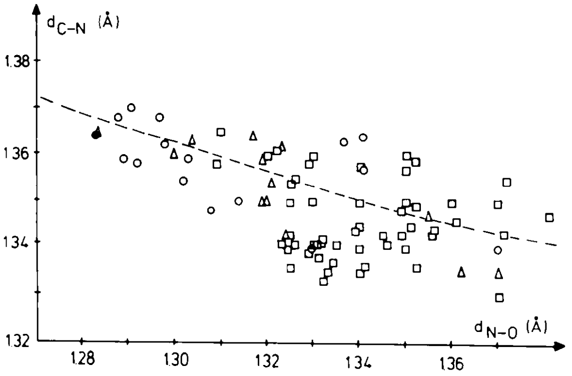

Fig. 1. Dependence of the C–N distance (d_{C-N}) on the N–O length (d_{N-O}) of pyridine *N*-oxides with NO groups involved in hydrogen bonds (triangles), in metal complexes (squares), and for the 'free' NO function (circles). The broken line has been calculated from (1) and (2) (see text).

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