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Letter

Structural principles of nitridoferrates: "isosteric" relations to main group systems*

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The crystal structures of nitridoferrates contain complex anions which are isostructural to main group systems: $^{1}_{\infty}[Fe^{III}N_{4/2}{}^{3-}]/SiS_2$, $[Fe^{III}N_3]^{6-}/[CO_3]^{2-}$, $[Fe_2^{II}N_4]^{8-}/[In_2P_4]^{6-}$, $^{1}_{\infty}[Fe_2^{II}N_3{}^{5-}]$/"$B_2S_3$" and $[Fe^{II}N_2]^{4-}/CO_2$. The nitridoferrate anions, moreover, satisfy "isosteric" principles, which is shown by the respective sequence $AB_2/16e^-$, $AB_3/24e^-$, $A_2B_4/32e^-$, $A_2B_3/24e^-$ and $AB_2/16e^-$. The number of electrons contributed from the transition element is consistent with its oxidation state. The remaining d^5/d^6 systems (Fe^{III}/Fe^{II}) are disregarded in this consideration. A survey of the concept together with structural details of the nitridoferrate anions which are known up to now is given in Fig. 1.

The low oxidation state and the linear coordination of iron in the anions $[Fe^{II}N_2]^{4-}$ establish the bridge to the low valent nitridocobaltates and nitridoniccolates, which also have a coordination number of two for the transition elements. The crystal structure of $Sr_2\{Li[CoN_2]\}$ [10] is an isotype of $Li_3[BN_2]$ [11] (approximately $Li_2\{Li[BN_2]\}$) and contains linear anions $[Co^IN_2]^{5-}$ which are isostructural and "isoelectronic" to $[Fe^{II}N_2]^{4-}$. Infinite chain anions $^{1}_{\infty}[NiN_{2/2}{}^{n-}]$ are present in the crystal structures of the low valency nitridoniccolates (*e.g.* Ba[NiN] [12], $Sr_3\{Li_3[NiN]_4\}$ [13] and (Ba_8N) $[NiN]_6$ [14]).

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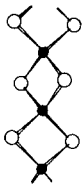
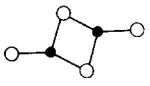
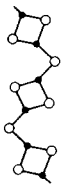
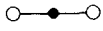
Compound, [Lit.]	Nitridoferrate-Anion/ Fe-N [pm]	"Isosteric" Relations
$Li_3[FeN_2]$, [1]	 196	$^1_\infty[Fe^{III}N_{4/2}{}^{3-}]$ 3+10+3=16(e^-) ---------(AB2)------ SiS_2, [7] 4+12=16(e^-)
$(Ca_3N)_2[FeN_3]$, [2] $Ba_3[FeN_3]$, [3] $Sr_3[FeN_3]$, [3]	 173-177	$[Fe^{III}N_3]^{6-}$ 3+15+6=24(e^-) ----------(AB3)----- $[CO_3]^{2-}$ 4+18+2=24(e^-)
$Ca_2[FeN_2]$, [4] $Sr_2[FeN_2]$, [4][a]	 183-190	$[Fe^{II}{}_2N_4]^{8-}$ 4+20+8=32(e^-) ----------(A_2B_4)---- $[In_2P_4]^{6-}$, [8] 6+20+6=32(e^-)
$Sr_2\{Li[Fe_2N_3]\}$, [5] $Ba_2\{Li[Fe_2N_3]\}$, [5]	 190	$^1_\infty[(Fe^{II}N_{3/2})_2{}^{5-}]$[b] 4+15+5=24($e^-$) ----------($A_2B_3$)----- "$B_2S_3$",[9][b] 6+18=24($e^-$)
$Li_4[FeN_2]$, [6] $Sr_2[FeN_2]$, [4][a]	 185-186	$[Fe^{II}N_2]^{4-}$ 2+10+4=16(e^-) ----------(AB2)------ CO_2 4+12=16(e^-)

Fig. 1. Nitridoferrate anions and "isosteric" relations to main group systems.
[a]The crystal structure of $Sr_2[FeN_2]$ [4] contains the anions $[Fe_2N_4]^{8-}$ and $[FeN_2]^{4-}$.
[b]The anion $^1_\infty[(FeN_{3/2})_2{}^{5-}]$ can be regarded as a section of the B_2S_3 layer structure [5, 9].

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($Ca_2[FeN_2]$: $C2/m$; $a=1093.0(2)$ pm, $b=496.0(1)$ pm, $c=684.4(1)$ pm; $\beta=121.09°$. $Sr_2[FeN_2]$: $P\bar{1}$; $a=653.8(1)$ pm, $b=869.0(2)$ pm, $c=893.2(2)$ pm; $\alpha=90.22(2)°$, $\beta=109.45(1)°$, $\gamma=102.30(1)°$.)
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(Sr_2{Li[CoN_2]}: $P4_2/mnm$; $a = 524.4(1)$ pm, $b = 730.7(2)$ pm.)
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