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The Influence of the Anionic Charge Density on the Coordination Number of the Lanthanide Cation

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Recently we reported a useful generalization, namely that the trivalent lanthanide cation prefers low coordination numbers in crystalline compounds in which the anionic charge is large [1]. Also recently we demonstrated that variations in the fusion temperatures of the lanthanide trihalides, LnX_3, where Ln = La–Lu, Y and X = Cl, Br, I are closely related to variations in the energetic stability of their crystal structures [2]. The generality of our treatment of the LnX_3 system is herein confirmed by its successful extension to include the lanthanide trifluorides LnF_3. More importantly, examination of the slopes of the linear relations between fusion temperature, T_f, and the lanthanide cation radius, r_i for LnF_3 in which Ln^{3+} is nonacoordinate (*vide infra*) and LnX_3 (X = Cl, Br, I) in which Ln^{3+} is either octa or nonacoordinate [2], does reveal that the destabilising influence of decreasing r_i is most critical to the LnF_9 coordination polyhedron and falls off in $LnX_{9,8}$ as Cl > Br > I. Steric considerations would have predicted an opposite trend even after the radius of I^- has been corrected for polarisation effects [2]. The versatility of thermal analysis in showing the subtle effects of the anionic charge density (which is largest in F^- and least in I^-) has afforded extended generality to the generalization stated above. Herein we report the rationale of this conclusion and restate the rule to accommodate the generality found in this study.

Values of the fusion temperatures (T_f) used are those tabulated by Greis and Haschke [3]; values of the cation radii (r_i) are those of Shannon and Prewit [4] and refer to Ln^{3+} in hexacoordination. Sources of structural data used are appropriately referenced in the text.

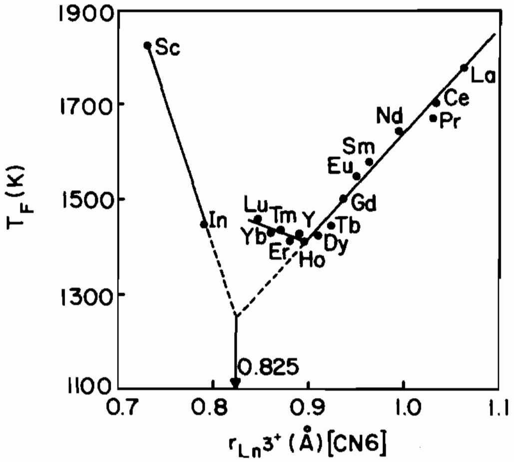

Fig. 1. Fusion temperatures, T_f, of LnF_3 *vs.* the cationic radii, $r_{Ln^{3+}}$ of the trivalent lanthanide.

Discussion

A plot of T_f *vs.* r_i for the lanthanide trifluorides, LnF_3, is given in Fig. 1; also included in Fig. 1 are the T_f values of the trifluorides of scandium and indium (ScF_3 and InF_3). As found in other lanthanide trihalides, LnX_3, The T_f values decrease to a minimum followed by an upward trend. However in this case the minimum occurs at Ho where a preference for octacoordination around Ln^{3+} rather than nonacoordination is significantly shown by the elongation of the ninth distance in the room temperature crystal structures [5]. The high temperature structures of these dimorphic LnF_3 show a switch from the LaF_3 structure ($P\bar{3}cl$) to the hexagonal/trigonal α-YF_3 structure between Ho and Er [3]; a corresponding minimum (Fig. 1) in the T_f *vs.* r_i plot is a clear indication that the two structures have different energy contents. Although full structure determination of the high temperature α-YF_3 modifications is not available to provide a definite picture of their lanthanide ion environment, it is reasonable to expect distortions in the α-YF_3 structure that would minimize repulsive forces (*i.e.* lower the effective coordination number of Ln^{3+}). An expulsion of the ninth anion from the coordination sphere of the Ln^{3+} cation in room temperature structures of LnF_3 is indicated by large differences between the average of the eight nearest LnF contacts and the elongating ninth Ln–F contact (0.20 Å in HoF_3 and 0.34 Å in YbF_3) [5]. There is no reason to expect that this trend will be radically changed in the high temperature modifications. Indeed, the fact that T_f increases with decreasing cation size in LnF_3 with the α-YF_3 structure is, from our previous study [2], an indication that the coordination number in these modifications

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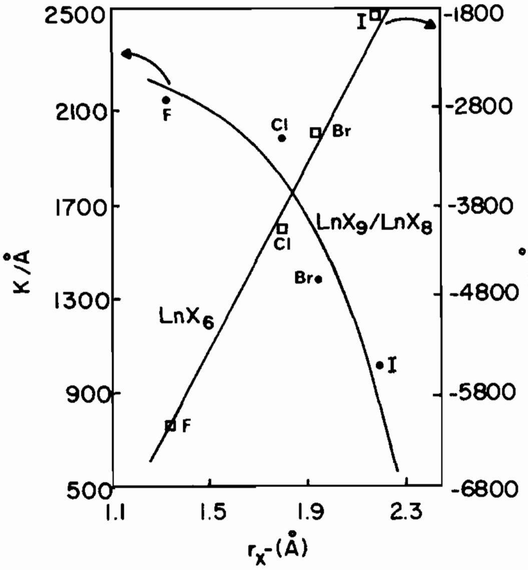

Fig. 2. Slopes obtained from the T_f/r_i plots *vs.* the halide anionic radii, r_{X^-} (see text).

is smaller than that found in LnF_3 with the LaF_3 structure; so that the increasing packing efficiency and Ln–F bond strength would account for the observed increasing trend in T_f for LnF_3 with Ln = HoLu. Inclusion of the trifluorides ScF_3 and InF_3 was prompted by an interesting observation that extrapolation of the line joining the Sc and In data points meets the least square line joining the data points La–Ho at r_i = 0.825 Å. Taking the F^- anionic radius to be 1.33 Å this value of r_i means that a switch from nona/octa coordination to hexacoordination in MF_3 compounds should be expected to occur at the radius ratio r^+/r^- = 0.62. This is the same ratio found to be applicable to $LnCl_3$ [2] and $LnBr_3$ if the radius of Br^- found empirically in UBr_3 is employed to calculate r^+/r^- [2]. Our results on these trihalide series are in good agreement with the value of 0.61 obtained by Garashina *et al.* [5] for the trifluoride system using unit cell parameters. There seems to be little doubt therefore that the radius ratio value of approximately 0.62 has significance in the structural chemistry of compounds of the trivalent lanthanides with monovalent ligands. It is our view that it is at this value of r^+/r^- that the anionic field is sufficiently strong to destabilise an eightfold or a ninefold coordination polyhedron.

The importance of the anionic field strength to the stability of the crystal structures of the lanthanide trihalide systems is further shown by the variations in the degree of destabilizing influence a decreasing r_i has on T_f. If the two parts of the V-curves (Fig. 1 and Fig. 1 of ref. 2) are subjected separately to linear regression we obtain slopes that are plotted against r_{X^-} in Fig. 2. Clearly a reduction in r_i has the largest impact on the LnF_3 compounds and the least on LnI_3 which is what is expected on the basis of anionic field effects rather than steric factors. Two synergistically related factors may promote rapid destabilization of high coordination polyhedra involving anions of high charge density: 1) for a given coordination polyhedron repulsive interactions will increase with decreasing size of the central cation and these interactions will be largest in polyhedra of anions with high charge densities; 2) if a polyhedron of a lower coordination number can be formed it is favored on account of increase in the bond strength and this increase is also largest for anions with high charge densities. Large anionic charge densities can be achieved either by keeping the formal charge constant but reducing the anionic size (as in the case of LnX_3; X = F, Cl, Br, I) or by increasing the formal charge of the ligating anions (as in the case of stepwise complexation $Ln_2Ox_3 \cdot nH_2O$, $LnOx_2^-$, $LnOx_3^{3-}$, and $Ln_2Ox_7^{8-}$ [1], where Ox = oxalate anion). It is therefore more instructive to restate the rule we reported earlier in a more general fashion afforded by the present investigation. Hence: 'The lanthanide cation prefers lower coordination numbers when the ligating anions exhibit large charge densities'.

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