Inorganica Chimica Acta, 140 (1987) 57–58

Borderline of Cluster Chemistry with Lanthanides*

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Abstract

Systems of discrete and isolated clusters frequently occur with 4d and 5d metals, but also with lanthanides. In their reduced halides, halide-carbides, -hydrides, -nitrides, the lanthanides exhibit a broad d metal chemistry with numerous condensed cluster phases. Due to the valence electron deficiency of these metals, the clusters are (with a few exceptions) stabilized by interstitial non-metal atoms which results in a borderline situation of salt-like compounds weakly stabilized by metal–metal bonding.

The term metal clusters makes one think of transition metals with d-electrons involved in metal–metal bonding. Such compounds are rather unexpected with lanthanides because of the low valence electron concentration of these metals. Yet there exists a broad d-metal chemistry of the rare earth metals with numerous M–M bonded compounds [1], which are closely related in structure and bonding to cluster compounds of the 4d and 5d metals. The common features of structure and bonding can easily be explained with compounds of the metals of the d-series, in particular with the valence electron-poor metals in the first half of these series.

To create M–M bonds, metal-centered valence electrons are needed. So the metal must be in a low oxidation state. In the elements themselves, M–M bonding is strongest with the metals Nb, Ta, Mo and W, as indicated by their high melting temperatures and large values of atomization energy. These metals also exhibit a rich metal cluster chemistry [2]. The halides of these metals in their lowest oxidation states are characterized by octahedral units of M atoms surrounded by halides in two characteristic ways, M_6X_8 and M_6X_{12}. The environment of 8 X atoms above all octahedral faces is preferred with 24 electrons in M–M bonding states (*i.e.* in 12 two-center, two-electron bonds along the edges of the octahedron), and 12 X atoms above all edges are preferred with 16 electrons filling the two-electron, three-center bonds in the octahedral faces. What happens in the case of electron deficiency? There are two ways out of the dilemma.

(i) The clusters are stabilized by interstitial atoms. The first such example found was Nb_6I_{11}, which absorbs hydrogen to form HNb_6I_{11}, thus formally increasing the number of electrons in M–M bonding states from 19 to 20 [3]. In reality the cluster is stabilized by building up a strong H–Nb multicenter bond at the expense of weak Nb–Nb bonds. One can extrapolate to the situation where all M–M bonds in a cluster are removed and only strong bonding with the interstitial atom is left.

(ii) Decreasing the number of non-metal atoms around the central octahedral M_6 unit finally leads to a condensation of clusters [4]. The kind of condensation which is most relevant to metal-rich rare earth compounds occurs via opposite edges of the M_6 octahedron. This type of condensation of (empty!) M_6X_{12} clusters is frequently found with reduced oxomolybdates. In the structure of $NaMo_4O_6$, infinite chains of condensed clusters occur [5]. Recently, it was demonstrated that the chain can be subdivided, leading to oligomeric clusters containing 4, 5 or 6 condensed Mo_6 octahedra [6, 7].

(i) and (ii) represent the structural principles in the chemistry of binary and ternary metal-rich halides of the lanthanides. The growing family of carbide halides (Table I) is especially suited to discuss these principles in terms of different degrees of condensation (isolated, oligomeric clusters, structures with 1D, 2D and 3D condensed clusters) and different types of interstitial atoms and molecules (C, C_2). Simple counting rules on the basis of an ionic model help in the understanding of the structural features [1]. They are in accordance with the results of band structure calculations for the special systems $Gd_{10}Cl_{18}C_4$ [8] ($x = 17, 18$) and $Gd_2Cl_2C_2$ [9]. Bonding in the carbide halides, as well as hydride halides or nitride halides of the lanthanides, is understood on a rather quantitative level.

Future work aims at the investigation of physical properties, especially magnetic interactions, of the

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*Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

This short paper seeks to reconstruct the 'red line' of the lecture presented at the International Conference on Lanthanides and Actinides, 2nd ICLA, in Lisbon. The matter discussed will be part of a detailed review to appear in the first issue of *Angewandte Chemie* in 1988.

0020-1693/87/$3.50

TABLE I. Gadolinium Carbide Halides

Compound	Structure	Distance (Gd–Gd) (pm)	C species	Number of metal-centered valence electrons per formula unit	Reference
$Gd_{10}Cl_{18}C_4$	2 Gd_6 octahedra joining an edge	321–409	C_2^{6-}	0	10
$Gd_{10}Cl_{17}C_4$		312–401	C_2^{6-}	1	10
$Gd_{10}I_{16}C_4$		328–400	C_2^{6-}	2	11
$Gd_{12}X_{17}C_6$ [a]	$^1_\infty$chain	319–427	C_2^{6-}	1	12
Gd_4I_5C		333–398	C^{4-}	3	11
$Gd_6X_7C_2$ [a]	$^1_\infty$twin chain	339–395	C^{4-}	3	11
Gd_3I_3C		331–391	C^{4-}	2	13
$Gd_2X_2C_2$ [b]	$^2_\infty$layer	345–400	C_2^{4-}	0	14
Gd_2Br_2C		343–382	C^{4-}	0	14
$Gd_6Cl_5C_3$		340–389	C^{4-}	1	13
Gd_2IC		338–386	C^{4-}	1	13
Gd_3Cl_3C	$^3_\infty$framework	329–368	C^{4-}	2	15

[a] X = Br, I. [b] X = Cl, Br, I.

low-dimensional bonding regimes of lanthanides in these new compounds. First results with Gd_2Cl_3, showing it is a 1D-Heisenberg antiferromagnet, look promising. A further extension of the chemical work is into the field of metal-rich compounds of actinides.

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