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Are metal alkoxides linear owing to electrostatic repulsion?

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Density functional theory calculations on [LnCp$_2$APh] (Ln = La, Lu; Cp = η^5-C$_5$H$_5$; A = O, S; Ph = C$_6$H$_5$) suggest that the linearity of the Ln–O–C vectors arises largely as a result of electrostatic repulsion between the α carbon and the trivalent metal centre.

Alkoxides (–OR) are an important class of ligands for the transition metals,[1–7] and consequently many workers have attempted to understand the factors governing the bonding in alkoxide complexes. It has long been known that, by contrast with their heavier congeners, terminal alkoxides usually bind in an essentially linear fashion.[8] Moreover, the M–O distances are invariably found to be significantly shorter than expected on the basis of the covalent radii. Most textbooks attribute these features to partial multiple bonding between the metal centre and the oxygen donor atom arising from π symmetry overlap of empty metal functions with the occupied p-orbitals on the ligand.[9]

Several groups have attempted to probe early transition metal alkoxides for structural evidence of such π interactions. Arguing that π donation should have geometrical consequences for the oxygen atom, both Rothwell[10] and Parkin[11] have plotted M–O distance as a function of M–O–R angle for Nb, Ta, and Zr complexes. No correlation was found. More recently we have plotted similar data for complexes of a typical lanthanide element, Sm, and also failed to find any correlation,[12] substantially weakening the argument for structurally significant π interactions. Parkin has suggested that the short Zr–O distance is due to the extra electrostatic contribution arising from the charge separation in the bond.[11] Such shortening has long been rationalized on the basis of the electronegativity difference between the atoms using the Shomaker–Stephenson equation.[13–17]

With regards to the M–O–R bond angle, Parkin provided evidence for this being a relatively soft potential subject to strong steric control, and noted that "at the extreme of a completely ionic interaction…a linear geometry would be anticipated".[11]

In considering the structures of these compounds we, like Parkin,[11] refer back to the structure of the group 16 hydrides for which a gradual decrease in the H–A–H angle is seen on going down the group: H_2O 104.5°, H_2S 92.2°, H_2Se 91.0°, H_2Te 89.5°. Pauling has argued that the bonding in such simple molecules arises essentially from overlap of the hydrogen atoms with the p-orbitals of the central atom.[13] The observed deviations from the theoretical 90° angle then arise simply from the electrostatic repulsion between the hydrogen atoms as a result of polarization of the A–H bonds by the electronegative central atom. Water shows the largest deviation from a right angle geometry as oxygen is the most electronegative chalcogen. Although Coulson pointed out that this valence bond view is overly simplistic,[18] and suggested that in water the H–O–H angle is determined partly by 2s/2p hybridisation, photoelectron spectroscopy studies highlight the importance of electrostatics in determining the structure of these small molecules.[19] Applying these simple arguments to transition metal and lanthanide chalcogenolates leads to the conclusion that while the kinked structures of the heavier chalcogenolates are uncontentious, the alkoxides are clearly anomalous.

With a view to gaining insight into the nature of the lanthanide chalcogenolate bond, and the structural differences between compounds of the different ligands, we have carried out quasi-relativistic gradient-corrected density functional theory calculations on the model system [LnCp$_2$APh] (Cp = η^5-C$_5$H$_5$; A = O, S; Ph = C$_6$H$_5$).† Calculations were restricted to the formally closed shell La(III) ([Xe]4f^0) and Lu(III) ([Xe]4f^{14}) systems (a growing number of studies confirm the f-orbitals to be of negligible importance in the bonding of trivalent lanthanide systems[24,25]). The S compound was chosen as being representative of the heavier chalcogenolates (similar calculations in which Ph is replaced by Me for A = O, S, Se, Te indicate that all three of the heavier group 16 compounds behave very similarly to one another). Full geometry optimisations were performed in C_s symmetry, with the plane of the Ph ring lying perpendicular to the molecular mirror plane. The total molecular bonding energy was subsequently calculated as a function of (i) the La–O–C^α–C^β dihedral angle ([LaCp$_2$APh] only) and (ii) Ln–A–Ph angle using the ADF 'linear transit' (restricted geometry optimisation) facility. Fig. 1 summarises the systems studied and the geometric distortions considered.

The optimised geometries successfully reproduce the key feature of the experimental structural studies, *i.e.* the oxo complexes are most stable at Ln–A–Ph = 180° while the S systems have much smaller angles (111° for La and 114° for Lu). Examination of the valence molecular orbital compositions and Mulliken overlap populations indicates that the extent of σ mixing between metal and chalcogen orbitals is extremely small (at most 10/90%) as would be expected for such an ionic system. Furthermore, the orbitals of Ln–A π symmetry are entirely localised on the chalcogen (*i.e.* are Ln–A non-bonding). This conclusion is reinforced by examination of the effect of rotating the alkoxide ligand in [LaCp$_2$OPh] around the La–O axis (distortion (i)). Essentially no variation in the total molecular bonding energy (<2 kJ mol^{-1} for rotation through 90°) was found as a function of this distortion, even though such a motion is expected to disrupt any conjugation between the aromatic system and the metal.‡ Taken together these observations would appear to rule out π interactions as significant contributors to the structure of lanthanide alkoxides.

In view of Pauling's comments regarding the structure of water, and Parkin's suggestion that alkoxide linearity may be influenced by electrostatics, we examined the charges on the metal centre, the donor atom, and the α carbon of the Ph group.

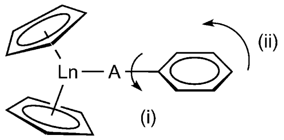

Fig. 1 Schematic representation of the [LnCp$_2$APh] systems studied. Ln = La, Lu; A = O, S. The phenyl ring lies perpendicular to the C_s mirror plane, which contains the A and Ln atoms, the 1 and 4 C atoms of the phenyl ring, and one C atom from each Cp ring. The arrows indicate the geometric distortions considered ((i) and (ii)—see text).

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These are collected for [$LaCp_2APh$] at La–A–Ph = 180° and 120° in Table 1. It is notable that the charges do not change significantly as the angle is reduced (distortion (ii)), suggesting that the nature of the metal–ligand bonding does not change during the distortion. Not surprisingly, the O–C bond of the alkoxides is much more polarized than that for A = S. Coupled with the fact that the α carbon is closer to the metal in the oxo complex than in the thiolate, we wondered whether, for the alkoxides, *a significant electrostatic repulsion occurs between the metal and the α carbon atom*. Calculation of the Coulombic interaction energy as a function of Ln–O–C^{α} angle reveals moderately strong repulsive potentials which map reasonably well (given the well-established sensitivities of Mulliken charges to computational parameters§) onto the total bonding energy curves for bending the alkoxides (data for [$LaCp_2APh$] shown in Fig. 2). By contrast no such electrostatic repulsion is seen for the corresponding thiolate complexes, as the charge on the α C atom is very close to zero. We therefore suggest that a secondary electrostatic interaction is a significant structural determinant for lanthanide alkoxides. Such a simple suggestion is both chemically appealing and consistent with the well-established view that bonding in lanthanide complexes is predominantly ionic.[26] It also accounts for the softness of the bending potential, since deformations of up to ±30° from linearity have only a small effect on the Coulombic energy. Furthermore, we note that all transition metal ROO^- complexes show sharp bending at the α oxygen, consistent with our expectations.[27]

In conclusion, we have presented evidence to support the suggestion that the linearity of alkoxides is a predominantly electrostatic effect. It is quite likely that imido complexes of the heavier transition metals are also subject to similar electrostatic contributions. Indeed, it is noteworthy that Cundari failed to find a significant correlation between bond length and angle in early transition metal imido complexes.[28] We believe, therefore, that much of the discussion of the bonding in linear *vs.* bent imido complexes[29] may have to be re-evaluated since the angle at nitrogen may simply reflect the different degrees to which charge builds up at the α carbon. Computational and synthetic studies are in progress to establish whether the conclusions drawn from the present target systems are indeed more widely applicable.

Table 1 Mulliken charges Q of the metal, the chalcogen and the α C atom in [$LaCp_2APh$] (A = O, S) at La–A–C^{α} angles of 180° and 120°

Compound	∠ La–A–C^{α}	Q(La)	Q(A)	$Q(C^{\alpha})$
[$LaCp_2OPh$]	180°	1.60	−0.81	0.44
	120°	1.58	−0.80	0.45
[$LaCp_2SPh$]	180°	1.39	−0.40	0.07
	120°	1.38	−0.40	0.01

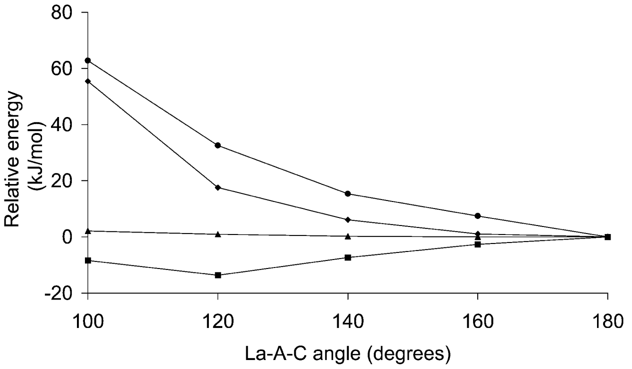

Fig. 2 Variation in total molecular bonding energy of [$LaCp_2APh$] (A = O, ◆; A = S, ■) and La/C^{α} Coulombic energy (A = O, ●; A = S, ▲) as a function of La–A–C^{α} angle (distortion (ii)). All data are normalised to an arbitrary zero at an La–A–C^{α} angle of 180°.

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Notes and references

† Calculations were performed using the Amsterdam Density Functional (ADF) program suite (versions 2.3 and 2000).[20] The basis sets employed were uncontracted, valence-only, Slater type functions of triple zeta quality. Two polarisation functions (one d and one f) were included for C, O and S (ADF Type V); one p function was added for H (ADF Type IV). Quasi-relativistic scalar corrections—Darwin and mass-velocity—were included *via* the Pauli formalism. The frozen core approximation was employed, and quasi-relativistic frozen 1s (C, O), 2p (S) and 4d (La, Lu) cores were calculated by the ADF auxiliary program 'Dirac'. The local density parameterisation of Vosko, Wilk and Nusair was used,[21] in conjunction with Becke's gradient correction[22] to the exchange part of the potential and the correlation correction due to Perdew.[23]

‡ Power has attempted unsuccessfully to search for an energy barrier to this process in aluminium alkoxides.[17]

§ Mulliken charges are very dependent on the choice of computational parameters, especially basis sets. We therefore repeated our calculations with different basis sets for all of the atoms in the target systems, and have analysed the results using not only the Mulliken charges, but also the Voronoi and Hirshfeld charges (which are also calculated by ADF). While the results naturally differed quantitatively, the qualitative conclusions are in all cases the same.

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