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Review

STERIC AND STEREOCHEMICAL ASPECTS OF METALLO-ORGANIC COMPOUNDS CONTAINING OXYGEN- OR NITROGEN-DONOR LIGANDS *

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Summary

The importance of the steric effects of bulky alkoxy or dialkylamido ligands in determining the physico-chemical properties of the metal alkoxides and metal dialkylamides is discussed. A range of interesting phenomena such as abnormal volatility and the stabilization of unusual oxidation states or coordination numbers, are shown to follow from the imposition of severe inter-ligand intramolecular repulsions in these metallo-organic compounds.

It gives me the utmost pleasure to participate in the celebration of Professor Ram Charan Mehrotra's 60th birthday by contributing to this splendid commemorative volume which is a most fitting way to review the great man's contributions to Inorganic Chemistry.

The purpose of this article is to give a brief account of the importance of the steric effects of organic ligands in influencing the structure and reactivity of inorganic compounds. It will come as no surprise to find that I shall be mainly concerned with the metal alkoxides and the metal dialkylamides.

It was through our fruitful collaboration in studies on the metal alkoxides at Birkbeck College over thirty years ago that I first became acquainted with Professor Mehrotra and forged an enduring friendship and respect. Our most recent and pleasant collaboration culminated in the publication of a monograph on the metal alkoxides [1]. A brief historical digression may not be out of place and might even be instructive to the younger generation of chemists. As a graduate in the immediate post-war period I was simultaneously aware on the one hand of the neglect of inorganic chemistry relative to organic and physical chemistry and on the other hand of the impact of Linus Pauling's great book "The Nature of the Chemical Bond". I was particularly fascinated by the effect of the nature of intramolecular bonding (i.e. ionic or covalent character) on

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* Dedicated to Professor R.C. Mehrotra on the occasion of his 60th birthday (February 16th, 1982).

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intermolecular forces and properties such as melting and boiling points of compounds. At the same time the development of the Hughes-Ingold theory for substitution reactions at a carbon centre made us aware of our ignorance of the mechanisms of reactions at metal centres in metal complexes. I was very impressed by the clear demonstration of the dramatic effects of bulky groups on the rates and course of reactions and also of the difficulty in disentangling steric from electronic factors in explaining the results.

I was confronted by this dilemma in attempting to interpret the physicochemical properties of the zirconium tetra-alkoxides which I had synthesized as part of my Ph.D. research. Thus $Zr(OCH_3)_4$ was an insoluble apparently non-volatile white solid, $Zr(OCH_2CH_3)_4$ was sparingly soluble in benzene and difficult (in those days!) to sublime (ca. 180°C at 10^{-4} mmHg), but $Zr[OCH(CH_3)_2]_4$ was soluble in benzene and could be distilled at 160°C at 0.1 mmHg whilst $Zr[OC(CH_3)_3]_4$, a colourless liquid, was so volatile (b.p. ca. 52°C at 0.1 mmHg) that is fumed in the air. Only the tetra-tert.-butoxide was a monomer, the others being increasingly polymeric with decreasing size of the alkyl group.

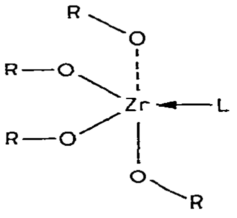
In terms of Sidgwick's concept of the Effective Atomic Number, the forerunner of the 18-electron valence shell for transition metals, it seemed abundantly clear that a monomeric 4-coordinated zirconium atom in $Zr(OR)_4$ was electronically unsaturated. Also it appeared that there were three mechanisms available for the zirconium atom to increase its share of electrons:-

(I) Add on more donor ligands (L) giving $Zr(OR)_4(L)_x$.

(II) Draw on the alkoxide oxygen lone pairs by bridging — i.e. polymerization $[Zr(OR)_4]_n$.

(III) Draw on the alkoxide oxygen lone pairs by intra-molecular π-bonding.

These modes of bonding are illustrated in I, II and III.



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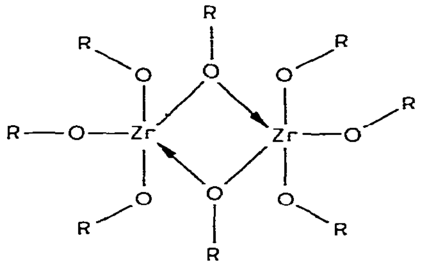

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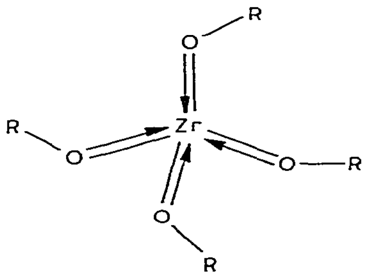

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It was clear that zirconium did not prefer mechanism I although a few complexes such as $\{Zr[OCH(CH_3)_2]_4[(CH_3)_2CHOH]\}_2$ and $\{Zr[OCH(CH_3)_2]_4(C_5H_5N)\}_2$ were known where I and II were both involved. The results were readily understood if II were the dominant process because it would obviously be susceptible to the steric hindrance of the alkyl group. Thus the bulky tertiary butoxide could not form alkoxide bridges and would be forced to assume a monomeric state which would accordingly be volatile. However, the electron-releasing tendency of the tert.-butyl group would also favour the π-bonding mechanism III which might support a monomeric species. Professor Mehrotra and I embarked on a systematic programme to explore the influence of the size and shape of the alkyl group on the properties of Group IV metal alkoxides.

This meant synthesizing a large number of non-commercially available secondary and tertiary alcohols before they could be used to synthesize the metal alkoxides. It was Professor Mehrotra's tremendous enthusiasm, skill and energy which alone made it possible for us to establish the fundamental basis of alkoxide chemistry several years before the advent of infrared and nuclear magnetic resonance spectroscopy, mass spectroscopy and ultimately rapid single crystal X-ray structure analysis.

I think we showed fairly conclusively that the steric effect of the alkyl group had a powerful effect in determining the degree of polymerization and hence the volatility of the metal alkoxide. Neopentyl alcohol, $(CH_3)_3C \cdot CH_2OH$, played an important role as a primary alcohol having a substantial steric effect. During this work we were surprised to discover that monomeric hafnium tertiary alkoxides were more volatile than their zirconium analogues in spite of the much greater mass of hafnium compared to zirconium. Due to the lanthanide contraction the atomic radii of these two elements are almost equal and the intermolecular forces in their monomeric tertiary alkoxides, which are mainly due to interactions of the peripheral alkyl groups, lead to virtually equal values for enthalpies of vaporization. Under these conditions the relative volatility of the zirconium and hafnium monomers appears to be determined by the effect of molecular mass on the entropy terms and makes the "heavier" species slightly the more volatile. Such considerations are also important in connection with the relative volatility of isotopic molecules [2].

I continued working in the metal alkoxide field after Professor Mehrotra returned to India and I was fortunate enough to have a series of very able Indian coworkers to explore a range of other metals. Eventually I attempted to rationalize the preferred degree of polymerization of a metal alkoxide in terms of possible structures and stereochemistry of the metal [3].

A feature of the d^0 metal alkoxides is their facile reactivity with hydroxylic molecules:-

$$M(OR)_x + x\,R'OH \rightarrow M(OR')_x + x\,ROH \qquad (1)$$

This reaction was powerfully effective in our Group IV metal alkoxide programme because it enabled us to synthesize the alkoxide $M(OR')_4$, where R'OH was a scarce or sensitive alcohol, starting from the pure metal isopropoxide. However, if R'OH was a highly branched tertiary alcohol the reaction in eq. 1 might be restricted by steric hindrance. These reactions and others using carboxylic acids, β-diketones, polyols and other hydroxylic ligands were pursued with greatest vigour by Professor Mehrotra and his coworkers in India. My group explored the controlled hydrolysis of the metal alkoxides, and we became involved in the structural implications of coordination-condensation polymers at a time increasing interest in the synthesis of inorganic polymers having high thermal stability.

This led me into the other area I would like to discuss, namely the metal dialkylamides $M(NR_2)_x$, which I developed with the able support of Dr. Ian M. Thomas at the University of Western Ontario in Canada. The idea was to synthesize inorganic polymers having a metal—nitrogen-bridged backbone and this produced some interesting transition metal chemistry [4].

It was soon evident that the steric effect of a ligand NR_2 was very much greater than that of OR, so that most of the new metal dialkylamides proved to be monomers. The π-donating tendency of the NR_2 ligand was also potentially greater than that of OR and this produced some interesting electronic considerations. For the early transition metals in oxidation state d^0, d^1, d^2 or d^3 it was possible to synthesize the binary dialkylamides $M(NR)_x$ as follows:

$$MCl_x + xLiNR_2 \rightarrow M(NR_2)_x + xLiCl \qquad (2)$$

The steric hindrance of the dialkylamido ligand manifested itself in the chemistry of chromium and led inexorably to my more recent interest in low coordination numbers.

Dr. J.S. Basi showed that the $CrCl_3/LiNEt_2$ reaction gave an unstable Cr^{III} diethylamide, $Cr_2(NEt_2)_6$, which disproportionated to produce the volatile monomeric Cr^{IV} derivative, $Cr(NEt_2)_4$ [4]. This was an unprecedented example in chromium chemistry, although it has recently been shown by Sir Geoffrey Wilkinson and his coworkers that the Cr^{IV} tetra-alkyls, CrR_4, can similarly be obtained if bulky alkyl groups are used. The very bulky dialkylamide NPr^i_2 led to the isolation of our first 3-coordinated compound of chromium.

$$CrCl_3 + 3LiNPr^i_2 \rightarrow Cr(NPr^i_2)_3 + 3LiCl \qquad (3)$$

The chromium tris-diisopropylamide was a deep brown, sublimable monomeric solid which was highly air sensitive and chemically reactive. Nevertheless, it was thermodynamically stable, as shown by the formation of the parent molecular ion and various fragment ions in the mass spectrometer, and it raised interesting questions such as the magnitude of the crystal field stabilization energy (CFSE) of a d^3 species in a trigonal field. Efforts to synthesize other $M(NPr^i_2)_3$ were unsuccessful and it was fortunate that Bürger and Wannagat [5] showed that the bulky silicon-containing bis-trimethylsilylamido ligand $N(SiMe_3)_2$ gave Cr^{III} and Fe^{III} compounds. The presence of the silicon atoms makes the nitrogen lone pair in $N(SiMe_3)_2$ potentially a weaker π-donor than in NPr^i_2 due to $N \rightarrow Si$: p_π—d_π interactions, and this may be important in helping to stabilize derivatives of d-electron-rich metals.

Since my return to London at Queen Mary College, my coworkers and I have embarked on a detailed investigation of the transition metal derivatives using the bulky NPr^i_2 and $N(SiMe_3)_2$ groups, with special reference to abnormally low coordination numbers [5]. We have been fortunate in enjoying the fruitful and enthusiastic collaboration of my colleague Dr. M.B. Hursthouse and his students who have elucidated the crystal structure of our compounds by X-ray diffraction. This is an essential basis on which to develop any theoretical framework for such unusual compounds. The most striking discovery came from the synthetic work of Dr. J.S. Ghotra, who isolated the series of crystalline lanthanide tris-silylamides, $Ln[N(SiMe_3)_2]_3$ [5]. Normally, the lanthanides are given to favouring the highest coordination numbers (eg. 9, 10, 11, 12) and it was doubtful whether these large trivalent ions could be constrained to a coordination number of 3. Although highly reactive to air and moisture, these compounds gave parent molecular ions and fragment ions in the mass spectrometer. The electronic absorption spectra of the Pr and Nd derivatives showed substantial splitting of the $4f$ energy levels [5] and recent ESR work on the Gd derivative revealed further evidence of the strong perturbation of the $4f$ levels in the intense trigonal field [6]. Interestingly, the X-ray crystal structures showed that Sc and the lanthanide tris-silylamides have a pyramidal configuration with the metal atom about 0.35 Å above the plane of the three nitrogens [5]. On the other hand, dipole moment and infrared spectral evidence suggests that in solution the lanthanide silylamides have a trigonal planar configuration. Further work showed that 4-coordinated lanthanide species could be obtained by adding triphenylphosphine oxide [5].

$$\mathrm{Ln[N(SiMe_3)_2]_3 + Ph_3PO \rightarrow Ln[N(SiMe_3)_2]_3(Ph_3PO)} \qquad (4)$$

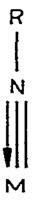
Work in progress suggests that the less steric demanding trimethylphosphine oxide may form both four- and five-coordinated complexes [7].

$$\mathrm{Ln[N(SiMe_3)_2]_3} + x\mathrm{Me_3PO} \xrightarrow{(x=1,2)} \mathrm{Ln[N(SiMe_3)_2]_3(Me_3PO)}_x \qquad (5)$$

These results have been demonstrated by observing the pseudo-contact-shifted NMR spectra of the Eu complexes which show enormous effects with change in symmetry around the paramagnetic ion.

Using bulky ligands we have isolated a range of 3-, 4-, and 5-coordinated metal species, e.g. $\mathrm{Cr(NO)(NPr^i_2)_3}$; $\mathrm{Cr[N(SiMe_3)_2]_3(THF)_2}$; $\mathrm{Mn[N(SiMe_3)_2]}$-$\mathrm{(THF)}_x$ ($x = 1$ or 2); $\mathrm{Cr_2(NO)_2(OPr^i)_6}$; $\mathrm{Co[N(SiMe_3)_2]_2(PPh_3)}$; $\mathrm{Ni[N(SiMe_3)_2]}$-$\mathrm{(PPh_3)_2}$; $\mathrm{TiCl[N(SiMe_3)_2]_3}$; $\mathrm{VO(NPr^i_2)_3}$; $\mathrm{TaCl_3[N(SiMe_3)_2]_2}$. This area of our work was reviewed in my lecture at the XXth meeting of the International Conference on Coordination Chemistry in Calcutta in 1979. We are currently attempting to evaluate the effects of steric hindrance in these crowded molecules by measuring their fluxional behaviour using variable temperature NMR and relating this data to the known bond distances and bond angles derived from the X-ray crystal structures.

Another area of current research concerns the organo-imido compounds $\mathrm{M(=NR)}_x\mathrm{X}_y\mathrm{L}_z$. The alkylimido group bears a formal resemblance to the alkoxo group which kindled my early interest in steric effects on metal coordination. Thus the alkylimido ligand may act as a terminal group which is linear (IV) or bent (V) or it may be double bridging (VI) or triple bridging (VII) like the alkoxo group.



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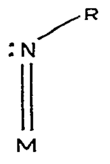

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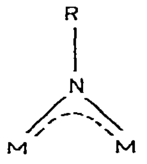

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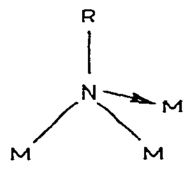

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We had made a number of polymeric titanium alkylimido compounds in Canada [9] where the bridging function was in evidence.

$$\mathrm{Ti(NR_2)_4 + 2R'NH_2 \rightarrow 1/}n\mathrm{[Ti(NR')_2]}_n\mathrm{ + 4R_2NH} \qquad (6)$$

Nevertheless, it was intramolecular congestion in the tantalum pentadiethylamide which produced our first monomeric alkylimido-metal compound [10].

$$TaCl_5 + 5LiNEt_2 \rightarrow Ta({=}NEt)(NEt_2)_3 + 5LiCl + Et_2NH + C_2H_4 \qquad (7)$$

Recently, Nugent and Harlow have prepared $Ta({=}NBu^t)(NMe_2)_3$ by the following elegant method:

$$TaCl_5 + 4LiNMe_2 + LiNHBu^t \rightarrow Ta({=}NBu^t)(NMe_2)_3 + 5LiCl + Me_2NH \qquad (8)$$

The crystal structure of $Ta({=}NBu^t)(NMe_2)_3$ shows the linear tert.-butylimido-tantalum moiety, suggesting the 4-electron donor behaviour of species IV [11]. The bulky silylamido ligand has also served to promote some other linear imido-tantalum species in some recent experiments [12].

$$TaCl_3[N(SiMe_3)_2]_2 + LiNHBu^t \rightarrow Ta({=}NBu^t)Cl[N(SiMe_3)_2]_2 + LiCl + HCl \qquad (9)$$

$$TaCl_3[N(SiMe_3)_2]_2 + 2Me_3SiBr \rightarrow$$
$$\tfrac{1}{2}\{Ta({=}NSiMe_3)(\mu_2\text{-}Br)Br[N(SiMe_3)_2]\}_2 + 3Me_3SiCl \qquad (10)$$

It is interesting to note that the dimeric bromo compound it is the bromide that acts as the bridging ligand and not the trimethylsilylimido group.

Whilst my own efforts have been mainly directed into the area of nitrogen-donor ligands I have never lost my interest in the metal alkoxides and it has been a continuing pleasure to watch the tremendous contributions of Professor Ram Charan Mehrotra in that field. His work on the double metal alkoxides has been especially fascinating and it is fitting that the symbol for these celebrations should be the lanthanide aluminium alkoxide $LnAl_3(OR)_{12}$.

In conclusion, I would like to say how delighted I am that my former research student Professor Malcolm Chisholm is contributing to this commemorative volume with his exciting results on molybdenum and tungsten alkoxides. This shows that the field of metal alkoxide chemistry which Ram Charan Mehrotra played such a vital role in revitalizing thirty years ago is still a rich source of interesting chemistry

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