Coordination Chemistry Reviews xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Lanthanide phosphine oxide complexes

Andrew W.G. Platt

School of Sciences, Staffordshire University, Leek Road, Stoke on Trent ST4 2DF, UK

ARTICLE INFO

Article history:
Received 25 August 2016
Received in revised form 21 September 2016
Accepted 21 September 2016
Available online xxxx

ABSTRACT

Phosphine oxide complexes of lanthanide metal have been studied to elucidate the fundamental aspects of their structural chemistry and to develop important technological applications mainly in the reprocessing of nuclear fuels and in photoluminescent devices but also in other fields such as gas sorption and homogeneous catalysis. The aim of this review is to give an overview of the range of complexes with phosphine oxides and trivalent lanthanide and yttrium ions, their structural features and applications.

Contents

1. Introduction and scope of the review

Complexes with phosphine oxides are an important area in the coordination chemistry of the lanthanide metals, not only from the fundamental aspects of the chemistry, but also from the wide range of applications which have been explored for these systems. This review covers developments principally from 2000 onwards although earlier work is mentioned to give context to the later studies and where further studies are limited. Early work on lanthanide complexes was reviewed in 1979 [1]. The studies established that nitrates form a variety of complexes with the composition $[Ln(NO_3)_3(R_3PO)_3]$ (R = Bu, Ph) being particularly favoured. Analysis of infrared spectra led to the conclusion that the metals were 9-coordinate with bidentate nitrates. Triphenylphosphine oxide was extensively studied and variation of reaction conditions allowed the isolation of $[Ln(NO_3)_3(Ph_3PO)_4]$ and $[Ln(NO_3)_2(Ph_3PO)_3]NO_3$. Lanthanide chloride complexes $[LnCl_3(Ph_3PO)_3]$ and $[LnCl_3(Ph_3PO)_4]$ were obtained for all lanthanides whilst the thiocyanate complexes $[Ln(NCS)_3(Ph_3PO)_4]$

Abbreviations: Acac, acetylacetonate; Bu, butyl; ^{i}Bi, isobutyl; ^{t}Bu, tertiary butyl; Bz, benzyl; CMPO, carbamoylmethylphosphine oxide; Cp, cyclopentadienyl; Cy, cyclohexyl; DMF, dimethylformamide; DMSO, dimethylsulfoxide; Et, ethyl; EXASF, Extended X-ray Absorption Fine Structure; Hp, heptyl; Hx, hexyl; Me, methyl; Oct, octyl; OTf, trifluoromethane sulfonate; Phen, 1,10-phenanthroline; Ph, phenyl; Prop, propyl; Pn, pentyl; ^{i}Prop, isopropyl.

E-mail address: a.platt@staffs.ac.uk

http://dx.doi.org/10.1016/j.ccr.2016.09.012
0010-8545/

Please cite this article in press as: A.W.G. Platt, Lanthanide phosphine oxide complexes, Coord. Chem. Rev. (2016), http://dx.doi.org/10.1016/j.ccr.2016.09.012

were obtained for the lighter metals whilst the smaller lanthanide ions form, presumably, 6-coordinate $[Ln(NCS)_3(Ph_3PO)_3]$. With the weakly coordinating perchlorate, ionic complexes $[Ln(ClO_4)_2(Ph_3PO)_4]ClO_4$ were isolated. The coordination chemistry of lanthanide and actinide halides with neutral oxygen and nitrogen donor ligands was reviewed in 2008, briefly covering phosphine oxide complexes [2]. The content here is ordered according to the number of PO groups in the ligand and then by lanthanide salt. The majority of early studies were on nitrate and halide complexes, but increasingly work on pentane-2,4-dionate complexes is being reported due to the interest in applications of these species to a number of fields. Yttrium has a very similar ionic radius to holmium and its chemistry, like that of the lanthanide metals is mainly that of the +3 oxidation state, and studies of this are also covered in the review. Organometallic complexes are not covered in this review.

2. The nature of the "P=O bond in phosphine oxides

Whilst the phosphorus oxygen bond in R_3PO is generally written as P=O its exact nature has been the subject of some debate. An early review summarised the conflicting opinions on the bonding phosphine oxides and concluded that a formal double bond between the phosphorus and oxygen atoms was the best description [3]. Subsequently more theoretical studies have suggested that the PO bond has a strong ionic component and is best represented as R_3P^+-O^- [4,5]. Experimental support for this formulation comes from ^{17}O solid state NMR studies on two polymorphs of Ph_3PO where the chemical shielding tensor and the ^{17}O quadrupolar coupling constant are consistent with its strongly ionic σ-bonded nature [6]. This is of significance to the bonding in lanthanide complexes which is expected to be predominantly electrostatic in nature between the negative O atom and the positively charged lanthanide ion. Also of significance would be the repulsion between the positively charged P and Ln centres which would be expected to make the Ln-O-P angle approach 180° in the absence of geometrical constrains imposed by the ligand, for instance in chelating structures, and secondary interactions in the peripheral structure of the complex.

The basicity of phosphine oxides is also of importance to their coordinating ability. In protic media the basicity is dominated by solvation effects on R_3POH^+ rather than the inductive effects of the substituents on the phosphorus atom. Thus for MeR_2PO the order of basicity with variation in R is Me > Bu > ^tBu [7]. In the gas phase the basicity follows the expected order of the inductive effect of the P-bound groups with the order in R_3PO being $^iProp_3PO$ > $^nProp_3PO$ > Et_3PO > Me_3PO [8]. The gas phase basicity may be more relevant to their metal coordination chemistry as the specific solvation interactions between R_3POH^+ and protic solvents are likely to be reduced in larger lanthanide complexes where any charge is spread over a larger surface area.

Bond distances within phosphine oxides will affect the steric requirements of the ligands. Structural data showing an increase in the PO distance along the series $M\varepsilon_2RPO$ (R = Me, Et, ^iProp, ^tBu) has been explained on the basis of molecular mechanics calculations as being due to increased steric repulsions and electronegativity effects which also increase the P–C(R) bond length [9].

3. Ligands with 1 PO group

3.1. Complexes with Lanthanide Nitrates

Complexes with trimethylphosphine oxide, Me_3PO and triethylphosphine oxide, Et_3PO, with $Nd(NO_3)_3$ have the composition $[Nd(NO_3)_3(R_3PO)_3]$ with the nitrate ions being assigned as $^2\kappa$ bidentate ligands on the basis of infrared spectroscopy [10]. The structure of $[Y(NO_3)_3(Me_3PO)_3]$ shows the metal to be 9-coordinate with $^2\kappa$ nitrates [11]. A useful description for these, and related 9-coordinate geometries, was given which considers the nitrates as pseudo-monodentate ligands [12]. On this basis $[Y(NO_3)_3(Me_3PO)_3]$ can be thought of as having a *fac*-octahedral structure. The displacement of nitrate by additional Me_3PO is possible giving the ionic $[Y(NO_3)_2(Me_3PO)_4]NO_3$. The effect of increasing the size of R_3PO has been subject to a systematic study using X-ray crystallography and variable temperature NMR spectroscopy. Triethylphosphine oxide gives $[Ln(NO_3)_3(Et_3PO)_3]$ for the lighter lanthanides which have a pseudo *mer*-octahedral geometry, presumably the increasing steric effect of Et_3PO compared to Me_3PO leading to the change from *fac* to *mer* structures [13]. The complexes of the heavier lanthanides were isolated as mixtures of $[Ln(NO_3)_3(Et_3PO)_3]$ and $[Ln(NO_3)_3(Et_3PO)_2]$ and the low temperature ^{31}P NMR spectra showed that a number of complexes exist in CD_2Cl_2 solution. These were assigned on the basis of the results from work with bulkier R_3PO (discussed below) as pseudo trigonal bipyramidal $[Ln(NO_3)_3(Et_3PO)_2]$ and *fac*- and *mer*-$[Ln(NO_3)_3(Et_3PO)_3]$.

For triisopropylphosphine oxide, $^iProp_3PO$, the pseudo *mer*-octahedral $[Ln(NO_3)_3(^iProp_3PO)_3]$ were isolated for Ln = La–Eu [14]. Variable temperature ^{31}P NMR measurements confirm that this geometry was retained in CD_2Cl_2 solution with a single signal at ambient temperature due to rapid exchange between inequivalent phosphorus environments splitting into 2 resonances with a 2:1 intensity ratio at lower temperatures. For erbium a pseudo *mer*-octahedral ionic complex $[Er(NO_3)_2(^iProp_3PO)_3(H_2O)]NO_3$ was characterised, whilst for heavier metals a pseudo trigonal bipyramidal complexes $[Ln(NO_3)_3(^iProp_3PO)_2]$ (Ln = Yb, Lu) were formed and structurally characterised.

Complexes with triisobutylphosphine oxide, $^iBu_3PO$, where the bulkier substituents are further removed from the immediate coordination site give pseudo *mer*-octahedral $[Ln(NO_3)_3(^iBu_3PO)_3]$ across the entire lanthanide series [15]. The dynamic NMR properties again show the geometry to be retained in solution and that the interconversion of inequivalent phosphine oxides is slower for the heavier lanthanides. Tritertiarybutylphosphine oxide, $^tBu_3PO$, forms only $[Ln(NO_3)_3(^tBu_3PO)_2]$ with 9-coordinate hydrates Ln = La–Nd and pseudo–trigonal bipyramidal complexes for the heavier lanthanides [16]. In the solid state the trigonal bipyramidal compounds exists as two isomers; one with an equatorial belt comprising either three essentially coplanar nitrates and linear PO-Ln-OP and the other with one of the nitrates twisted out of the equatorial plane and a non-linear PO-Ln-OP arrangement. The structures adopted in the Lu complex are shown in Fig. 1.

Tricyclohexylphosphine oxide, Cy_3PO, which has a similar bulk to $^tBu_3PO$ based on the cone angles of the respective phosphines [17] gives $[Ln(NO_3)_3(Cy_3PO)_3]\cdot xEtOH$ the structures of which show subtle effects due to the lanthanide contraction [18]. All the complexes have the pseudo *mer*-octahedral arrangement with the lattice ethanol (where present) hydrogen bonded to an oxygen of the coordinated nitrate. With the heavier metals there is an increased tendency to relieve steric strain caused by the lanthanide contraction by forming monodentate nitrates. Thus the structure of $[Er(NO_3)_3(Cy_3PO)_3]$ has two molecules in the unit cell, one with three $^2\eta$ nitrates and one with two $^2\eta$ one $^1\eta$ nitrate, whilst the Tm and Yb complexes have two $^2\eta$ and one $^1\eta$ nitrate as shown in Fig. 2.

Complexes of tributylphosphine oxide, $^nBu_3PO$, and trioctylphosphine oxide, Oct_3PO, have the composition $[Ln(NO_3)_3(R_3PO)_3]$ [19]. Analysis of the infrared spectra led to the conclusion that ionic nitrate was present. A study of the complex formation of $Nd(NO_3)_3$ with various organophosphorus reagents in supercritical CO_2 concluded on the basis of electronic spectroscopy that $[Nd(NO_3)_3(^nBu_3PO)_5]$ was formed, but no materials were isolated and further characterisation was not given [20]. Trioctylphosphine

Please cite this article in press as: A.W.G. Platt, Lanthanide phosphine oxide complexes, Coord. Chem. Rev. (2016), http://dx.doi.org/10.1016/j.ccr.2016.09.012