



Review

A theoretical analysis of ambivalent and ambiphilic Lewis acid/bases with symmetry signatures



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ABSTRACT

This review provides a theoretical underpinning of previously published definitions of ambidentate, ambivalent and ambiphilic ligands. The study encompasses ambivalent ligands such as NO, NR, N₂R; ambiphilic molecules such as SO₂, I₂ and ambiphilic transition metal complexes, e.g. [Pt(PCy₃)₂]. These ambivalent molecules adopt alternative geometries which depend primarily on the number of electrons which they formally donate or accept. The theoretical analysis focuses initially on those complexes where the same ligand displays ambivalent properties within the same molecule in order to define the energetics of their interconversion. These square-pyramidal complexes provide a test-bed for generating data which throws light on the relative abilities of ambivalent ligands to adopt linear or bent geometries. The ligands were compared with NO and their relative abilities were placed in the following order PO > PH₂ > N₂H > SO₂ > NO > NH₂ > NS. The linear nitrosyl ligand does not exert a *trans*-influence and this property has been contrasted with the nitrido-ligand which shows a large *trans*-influence. The conversion of NO to a non-linear geometry results in a strong *trans*-influence and this has significant catalytic and biological importance. Calculations on octahedral palladium complexes have been used to order the *trans*-influences of ambivalent ligands when they adopt their alternative symmetry signatures. The relative *trans*-influences are NO > PH₂ > NS > N₂H > NH₂. The interconversion of linear and bent dinitrosyls provides an interesting inorganic example of *valence tautomerism* and this is noted as a general characteristic of ambivalent and ambiphilic ligands. The soft energy surface associated with these interconversions leads to the experimentally verified fluxional process. The energetics of adduct formation by ambiphilic ligands has been studied using a series of SO₂ complexes of palladium and platinum and the results contrasted with adducts of SO₂ with main group Lewis acids and bases. The isomers {(PH₃)₂M(SO₂)*p*}¹⁶ and {(PH₃)₂M(SO₂)*np*}¹⁴ are calculated to have very similar energies and the relative stabilities of analogous isomers may be manipulated by varying the bite angle of the phosphine ligands in {(PH₂)₂C_nH_{2n}]M(SO₂)}. © 2015 Elsevier B.V. All rights reserved.

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1. Introduction

The initial extension of the Lewis bond description to Werner coordination compounds by Sidgwick was based on the assumption that the ligand is an electron pair donor to the Lewis acidic metal cation. As co-ordination chemistry has developed it has become increasingly clear that this description of the metal-ligand bond is an oversimplification. Ligands may enter into multiple bond interactions and indeed metals may also donate electron pairs to Lewis acids [1–5]. Pauling [6] was the first to articulate the idea that ligands such as CO are able to function simultaneously as a Lewis acid and Lewis base, when co-ordinated to transition metals in low oxidation states. These synergic interactions involve complementary σ and π orbitals on the ligand and metal and the point group symmetry of the adduct remains essentially unaffected by the relative contributions of the forward and back donation components, although the relative lengths of the M–C and C–O bonds do change [1]. The formal two-electron donating abilities of ligands such as CO remains constant from complex to complex, but variations in the forward and back donation components can change the electron distribution in the metal-ligand moiety and influence the reactivities of the complexes with nucleophiles and electrophiles. Changes in the oxidation state, co-ordination number, steric effects and the donor/acceptor properties of the “spectator” ligands have been used to fine-tune these reactivity trends.

In a recent review [7] I have drawn attention to the common characteristics of ligands which are capable of adopting alternative geometries, because of their ability to vary the number of electrons which they formally donate to the metal. The differences between *ambidentate*, *ambivalent* and *ambiphilic* ligands have been clarified and a notation has been developed which may be used to define the alternative geometries they adopt when co-ordinated to transition metals. A summary of this notation is provided in Appendix and the reader is directed to Ref. [7] for a fuller description of the proposals and specific examples of its applications. The notation is equally applicable to ligands which are π -acceptors and π -donors. This similarity between π -donor and acceptor ambivalent ligands has been understated previously. The ambivalent character of other π -acceptor and π -donor ligands is summarised in Table 1 and illustrated in Fig. 1. The alternative geometries adopted by these ligands may be related in the first instance to the electron donating and accepting abilities of the ligands within the traditional valence bond framework as shown in Fig. 1. Whilst this methodology, when used with the 18 electron rule, provides a satisfactory mode of accounting qualitatively for the alternative geometries of the majority of complexes, it fails to provide a satisfactory description of complexes with intermediate geometries, the relative energies of the

isomers with the alternative geometric forms, the effects of the alternative geometries on the other metal-ligand bonds and the consequences on the reactivities of the complex. The aim of this review is to provide a deeper insight into the bonding properties of ambivalent and ambiphilic ligands within a molecular orbital framework. The DFT methodology used for this theoretical analysis is described in more detail in Appendix.

Although this review aims to provide a more detailed understanding of the broad class of ligands which exhibit ambivalent and ambiphilic properties it is hoped that the conclusions derived from the analysis may also have implications for understanding the roles of such ligands in catalytic and biological processes. The discovery that nitric oxide has many roles in biology has resulted in an exponential growth of research into its chemistry and biochemistry. This has included detailed studies of a wide range of nitrosyl transition metal complexes of iron and copper with ligands which resemble those found in biology [8,9]. It has also renewed interest in the co-ordination chemistries of a range of the related SO₂, H₂S, CO, COS and N₂O molecules, which may also function as neurotransmitter molecules in biology [8–10]. When these *gasotransmitters* co-ordinate to transition metals they trigger subtle, but important, changes in the effective size of the metal (*via* spin changes), changes in the protein environment, *via trans*-influence effects, and the modulation of the redox properties of the metalloprotein. Understanding in molecular terms the mode of action and selectivity of the interactions between nitric oxide, dioxygen, etc and metalloproteins is fundamental. Specifically it is important to understand those factors which enable ligands to alter their geometries on coordination to transition metals and the impact on the conformations and subsequent reactions of metalloproteins. Basolo and his co-workers' [11] seminal mechanistic studies on complexes, which contain ligands capable of varying the number of electrons which they donate to the metal, established that they proceed by a different mechanism to that established previously for carbonyl complexes. They proposed that the transfer of an electron pair to the ambivalent ligand was associated with the bending process and opens up an empty orbital on the metal and thereby facilitates a bimolecular nucleophilic substitution reaction at the metal. In recent years Berke and his co-workers [12] have established the catalytic implications of this proposal for interpreting and enhancing the catalytic reactions of metal nitrosyl complexes.

The description of the properties of these ligands has clear implications for understanding their catalytic and biological effects. It is therefore necessary to provide clear definitions of the different classes of ligands and understand their structural and electronic properties at a molecular level. Although specific detailed molecular orbital calculations have been reported for a wide range of ambiphilic and ambidentate ligands and used to interpret their geometries and specific aspects of their reactions [13–34] there has been no attempt to understand in more general terms their electronic and structural features.

An *ambidentate ligand* has two or more Lewis base sites with potential donor capabilities. Generally these are lone pairs on alternative donor atoms, e.g. SCN[−] or NCS[−], but one of the isomers may involve donation from a π or σ bond, e.g. O₂ or H₂. Donation of electron pairs from these alternative sites may lead to different atom sequences in the complex and different symmetries, although in each isomer the EAN count is identical [1,7].

An *ambivalent ligand* is capable of forming more than one bond to a transition metal by donating a variable number of electrons. In these complexes the initial donor-acceptor bond is supplemented by donation from lone pairs on the donor atom to empty orbitals on the metal. These multiple interactions lead to multiple metal-ligand bonds and the dative π -component is enhanced by adopting a higher symmetry geometry (linear or planar usually). These ambivalent ligands are therefore associated with a symmetry

Table 1
Summary of the electron donating capabilities of ambivalent ligands with symmetry signatures.

Ligand	M-L geometric description (<i>descriptor</i>)	Electron donation
NO,NS	Linear (<i>l</i>)(180–160°)	3 electrons
NO,NS	Bent (<i>b</i>)(100–140°)	1 electron
NR ₂ (PR ₂)	Non-planar (<i>np</i>)	1 electron
NR ₂ (PR ₂)	Planar (<i>p</i>)	3 electrons
NCR ₂ (PCR ₂)	Linear (<i>l</i>)	3 electrons
NCR ₂ (PCR ₂)	Bent (<i>b</i>)	1 electron
N ₂ R	Linear (<i>l</i>) or Singly bent (<i>sb</i>)	3 electron
N ₂ R	Doubly bent (<i>db</i>)	1 electrons
N ₂ R	π -bonded (η^2)	3 electrons
NR	Linear (<i>l</i>)	4 electrons
NR	Bent (<i>b</i>)	2 electrons
NOR	Linear (<i>l</i>)	4-electrons
NOR	Bent (<i>b</i>)	2 electrons
OR	Bent (<i>b</i>)	1 or 3 electrons
OR	Linear (<i>l</i>)	5 electrons

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