Coordination Chemistry Reviews 254 (2010) 1357

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

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

Preface

Dithiolenes and non-innocent redox-active ligands

Combining transition metals with non-innocent ligands gives rise to coordination compounds with highly unusual physical properties and rich redox-chemistry. Both the metal and the ligands can exist in several oxidation states, presenting a challenge to theoretical chemistry. The ambiguity in electron distribution provides a means of controlling or switching molecular properties either electrochemically, optically, or structurally by substrate coordination. Research on non-innocent ligand complexes touches some basic chemical concepts such as oxidation state or electron delocalization, and influences how we think about transition metal chemistry and how we teach it. What had begun in 1960s as predominantly electrochemical and spectroscopic research on metal dithiolenes has evolved over the years into a major research area in coordination chemistry, with strong impact on catalysis, materials research and bioinorganic chemistry.

Besides their fundamental chemical importance, metal complexes of non-innocent ligands are very promising building blocks for functional molecular materials and, as such, they became one of the central research themes of the European scientific collaboration program COST Action D35 “*From molecules to molecular devices*”. This *Coordination Chemistry Reviews* special issue collects contributions presented at the COST D35 conference “*Dithiolenes and non-innocent redox-active ligands*”, which was organized by M. Fourmigué and C. Mitsopoulou in Vravrona (Greece) in June 2009. This meeting provided a comprehensive overview of the current status of non-innocent ligand chemistry as well as related research activities within the COST D35 Action. Investigating electronic structures using advanced spectroscopic, electrochemical and DFT quantum chemical techniques remain an important research direction, being used both to gain fundamental understanding (*Sproules and Wieghardt*, *Záliš*, *Lever*, *Fourmigué*) as well as to predict optical properties, namely nonlinear activity (*Mitsopoulou*, *Deplano*, *de Bonneval*). It is interesting to see the emergence of new types of non-innocent ligands such as polynitriles, oxazolines, o-aminothiolates, diselenolenes, dithiolenes derivatized with thiophene or tetrathiofulvalene (*Gomez-Garcia*, *Almeida*, *Avarvari*, *Llusar*), as well as extending the non-innocence concept to small ligands such as dioxygen or nitrous oxide (*Kaim*). Design rules for solid-state materials and layered organic/inorganic hybrids based on transition metal complexes with chalcogenolene ligands are set by *Mercuri*, who has applied them to develop new magnetic compounds and molecular magnetic conductors. Dithiolene-based clusters and polymers, including chains, layers and 3D-architectures, emerge as another type of promising materials with intriguing optical and redox properties (*Dalgleish and Robertson*, *Almeida*, *Llusar*). Molecular magnetism, spin-crossover and bistability (*Almeida*, *Marchivie*, *Gomez-Garcia*) as well as electrooptical behavior and conductivity (*Mercuri*, *Llusar*, *de Bonneval*) are strongly pursued, aiming at new functional materials. Last but not least, the important roles played by non-innocent ligands (dithiolene-coordinated pterines, tyrosine, flavines, tetrapyrroles, etc.) in biology are stressed by *Garner* and *Kaim*, whose contributions also show how our understanding of enzyme functions stimulate coordination chemistry. By and large, it is clearly demonstrated that chemistry of dithiolenes and other types of redox-active ligands remains a very active research area progressing towards new functional molecular materials and advancing our chemical and biological understanding.

Antonin Vlcek
Chair, COST Action D35
Queen Mary, University of London, SBCS,
Mile End Road, London E1 4NS,
United Kingdom
E-mail address: a.vlcek@qmul.ac.uk

9 December 2009

doi:10.1016/j.ccr.2010.01.015