



Review

Luminescent Ni(0) complexes

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ABSTRACT

With its $3d^{10}$ valence electron configuration Ni(0) is isoelectronic with Cu(I). While many Cu(I) complexes emitting from metal-to-ligand charge transfer (MLCT) excited states have been explored, the number of luminescent Ni(0) complexes known to date is very limited. Ni(0) is typically stabilized by carbonyls, phosphines or isocyanides due to the π -acceptor properties of these ligands, and photoluminescence has been reported in a few selected cases that are reviewed herein. Recent studies indicate that chelating isocyanide ligands are promising for obtaining Ni(0) complexes with long-lived 3 MLCT states, and this could be interesting for a similar range of applications as with photoactive Cu(I) complexes, including for example luminescent devices, solar cells, and organic photoredox reactions.

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1. Introduction

The photophysics and the photochemistry of Cu(I) complexes with long-lived 3 MLCT excited states have received significant attention over the past few decades [1–4]. Cu(I) is an attractive earth-abundant alternative to traditional d^6 3 MLCT emitters made from precious metals such as Ru(II), Re(I), Os(II), and Ir(III) [5]. While many initial studies of emissive Cu(I) complexes focused on basic photophysical aspects such as the distortion in the MLCT excited states [6–9], more recent studies tend to put a stronger emphasis on possible applications. This includes for example the use of Cu(I) complexes as luminophores in light emitting devices

[10,11], as dyes in solar cells [12], and as sensitizers for organic photoredox conversions [4,13,14]. At the same time, isoelectronic Ni(0) complexes have received very little attention, despite the fact that similarly favorable excited-state properties could be anticipated. Herein we provide a survey over the currently known luminescent Ni(0) complexes and discuss their properties in the context of other MLCT emitters made from earth-abundant metals.

2. From early structural studies to emissive complexes

The low oxidation state of Ni(0) asks for stabilization by π -acceptor ligands such as carbonyl, isocyanides, phosphines, or phosphites. Ni(CO)₄ can be considered the prototype of a tetrahedral Ni(0) complex and some analogous isocyanide complexes have long been known [15–17]. Early infrared spectroscopic studies demonstrated that isocyanides can indeed simultaneously act as good σ -donors and π -acceptors to Ni(0). These initial IR studies also indicated that the actual point symmetry of the Ni(CNC)₄

Abbreviations: dbiy, 1,3-di-*t*-butylimidazol-2-ylidene; dpp, 2,9-diphenyl-1,10-phenanthroline; dppe, 1,2-bis(diphenylphosphino)ethane; MLCT, metal-to-ligand charge transfer; NHC, N-heterocyclic carbene; PPh₃, triphenylphosphine; P(OPh)₃, triphenylphosphite; P(O-*o*-cresyl)₃, tri(*o*-xylyl)phosphite.

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groupings in homoleptic complexes with monodentate isocyanide ligands is lower than T_d , compatible with the view that the $M-C-N-C$ entities are nonlinear as a result of the metal-carbon π -bonding [18]. Initial studies focused on tetrakis(arylisocyanide) complexes of Ni(0), whereas tetrakis(alkylisocyanide) complexes became accessible in analytically pure form somewhat later [19,20]. Crystallographic studies of different tetrakis(arylisocyanide)nickel(0) complexes provided direct evidence for the anticipated slightly distorted structures [21,22], and in one rather special case a macrocyclic tetra-arylisocyanide complex of Ni(0) was reported [23]. More recent studies of Ni(0) isocyanide complexes have focused on coordinatively unsaturated Ni(CNR)₃ complexes as isolable analogues of unsaturated metal carbonyls, such as for example Ni(CO)₃ or Fe(CO)₄ [24–27]. However, the potential luminescence properties of Ni(0) isocyanide complexes did not seem to receive any attention until very recently [28].

By contrast, luminescent Ni(0) phosphine complexes were already reported by Dori and co-workers nearly 50 years ago [29]. The respective early study explored more than 50 different d^{10} metal complexes with phosphine and arsine ligands. In addition to Ni(0), complexes with several other d^{10} metals were investigated, including Pd(0), Pt(0), Cu(I), Ag(I), Au(I), Zn(II), Cd(II), and Hg(II). The study reported that, in the solid state at 77 K, all of these complexes exhibited luminescence after irradiation with a mercury-vapor lamp, although quenching was observed for Ag(I), Au(I), Cd(II), and Hg(II) at higher temperatures [29]. The general structure of the Ni(0) complexes was as represented in Scheme 1a with R^1 = phenyl or substituted phenyl and R^2 = aryl, alkyl, cycloalkyl and alkoxy. Unfortunately, actual luminescence spectra of Ni(0) complexes were not shown in this short communication. However, it was noted that the emission is likely due to $d \rightarrow \pi^*$ charge-transfer type excitations [29].

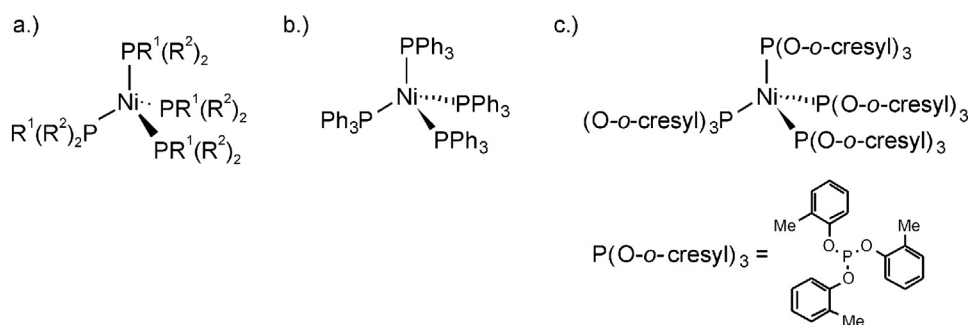
The first report of Ni(0) phosphine and phosphite complexes which possess long-lived emissive excited states in fluid solution at room temperature appeared in 1985 [30]. THF solutions of Ni(PPh₃)₄ and Ni(P(O-*o*-cresyl)₃)₄ (Scheme 1b, c) were reported by Caspar to show luminescence with band maxima at 740 and 645 nm, respectively. For the latter, an excited-state lifetime of 5.13 μ s and a luminescence quantum yield of 0.293% in N₂-saturated THF solution at 25 °C was reported [30]. However, several lines of evidence indicated that in the investigated class of NiL₄, PdL₄, and PtL₄ complexes the luminescence originates from species that are three-coordinate in both the ground and excited states. This interpretation made sense, since it was known that in solution the respective ML₄ complexes exist in equilibrium with ML₃ and ML₂ species. Luminescence quantum efficiencies were found to decrease upon addition of excess ligand, compatible with the view that coordinatively unsaturated species are the emitters. Organic triplet acceptors did quench the luminescence with rates depending systematically on the triplet energies of the organic acceptors, indicating that the emission originates from triplet states. The

relative insensitivity of the observed emission spectra to the nature of the phosphine, phosphite, and arsine ligand for a given metal (either Ni(0), Pd(0), or Pt(0)) suggested that the excited state is largely metal-localized in character. Based on extended Hückel calculations it was hypothesized that the lowest excited state for planar ML₃ d^{10} complexes involves the promotion of an (n) d -electron to a vacant metal-localized ($n+1$) p -orbital [30]. In light of studies on Cu(I) complexes it seems possible that THF solvent molecules can weakly coordinate to these ML₃ complexes [9].

The next report on luminescent Ni(0) complexes appeared 12 years later in a comparative study of Ni(dppe)₂, Ni(CO)₂(SbPh₃)₂, and NiL₄ with L = AsPh₃, SbPh₃, P(OPh)₃ by Frem and coworkers [31]. These complexes were synthesized from a Ni(II) source using NaBH₄ as a reducing agent. Ni(AsPh₃)₄ could be stored in stoppered vials for 3 years, Ni((OPh)₃)₄ was found to decompose over the period of a few days, and Ni(SbPh₃)₄ decomposed instantly when exposed to air. All complexes exhibited orange luminescence in the solid state and in fluid solution at room temperature. From the solid-state excitation and emission spectra in Fig. 1 it is seen that there are fairly large Stokes shifts of ca. 11,000 cm^{-1} , and this was interpreted in terms of luminescence from a spin-forbidden transition. Given the π -accepting characters of the ligands, the emissive excited state was assigned to ³MLCT. Luminescence lifetimes could not be determined due to instrumental limitations.

The structurally related Ni(CO)₂(PPh₃)₂ complex was investigated in the year 2000 by Kunkely and Vogler [32]. Compared to Ni(CO)₄ which exhibits efficient photodissociation, the heteroleptic Ni(CO)₂(PPh₃)₂ complex was found to be relatively stable. Following excitation at 356 nm, the complex showed red emission with a band maximum at 650 nm (dotted line in Fig. 2) both at room temperature in fluid acetonitrile and at 77 K. At such low temperature, the luminescence quantum yield was 10⁻³. The excitation spectrum roughly matched the absorption spectrum (solid line in Fig. 2). Similar to the complexes discussed above, there is a large shift between the emission band maximum and the maximum of the energetically lowest detectable absorption band. It was noted that in principle the lowest energy transitions could be either MLCT or intraligand (IL) transitions on the arylphosphine ligands (as observed previously in some Cu(I) arylphosphine complexes), but the assignment to ³MLCT states was favored. From the very large shift between absorption and emission (Fig. 2) it was inferred that excitation to the emissive state is associated with a considerable structural change, in analogy to what is commonly observed for Cu(I) polypyridyl complexes upon MLCT excitation.

In 2003 the same investigators reported on an interesting conceptual advance from phosphine to *N*-heterocyclic carbene (NHC) ligands (Scheme 2), leading them from the previously investigated Ni(CO)₂(PPh₃)₂ to the new Ni(CO)₂(dbiy)₂ complex (dbiy = 1,3-di-*t*-butylimidazol-2-ylidene) [33]. NHC ligands are comparatively weak π -acceptor ligands and hence MLCT transitions are expected to occur at higher energies than with phosphines. Indeed, the



Scheme 1. Molecular structures of some Ni(0) complexes investigated in the context of luminescence in the early literature [29,30].

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