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Author(s): Salojärvi, Esko; Peuronen, Anssi; Huhtinen, Hannu; Vlasenko, Leonid S.; Halme, Janne; Mäkinen, Pyry; Lastusaari, Mika; Lehtonen, Ari

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NIR-absorbing transition metal complexes with redox-active ligands

Esko Salojärvi,^a Anssi Peuronen,^{a,b} Hannu Huhtinen,^c Leonid S. Vlasenko,^{ce} Janne Halme,^d Pyry Mäkinen,^d Mika Lastusaari^a and Ari Lehtonen^{a*}

^aInorganic Materials Chemistry research group, Department of Chemistry, University of Turku, FI-20014 Turku, Finland

^bDepartment of Chemistry, P.O. Box 35, University of Jyväskylä, FI-40014 Jyväskylä, Finland

^cWihuri Physical Laboratory, Department of Physics and Astronomy, University of Turku, FI-20014 Turku, Finland

^dNew Energy Technologies, Department of Applied Physics, Aalto University, P.O. Box 15100, FI-00076 Aalto, Finland.

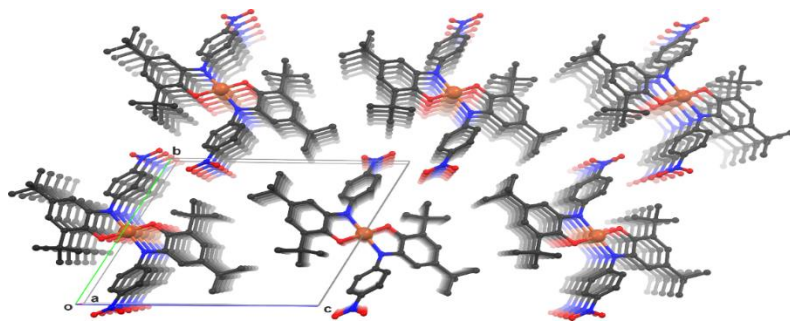
^eIoffe Institute, Russian Academy of Sciences, St. Petersburg 194021, Russia

Abstract

Best top stable transition metal (M = Co, Ni, Cu) complexes with a non-innocent *ortho*-aminophenol derivative were synthesized by the reaction of metal(II)acetates with a ligand precursor in 2:1 ratio. The solid-state structures reveal the formation of neutral molecular complexes with square planar coordination geometries. The Co(II) and Cu(II) complexes are paramagnetic, whereas the Ni complex is a diamagnetic square planar low-spin Ni(II) complex. All complexes, and Ni(II) complex in particular, show strong absorption in the near-IR region.

Graphical abstract

Co, Ni and Cu complexes with a non-innocent *ortho*-aminophenol were synthesized by the reaction of metal(II)acetates with a ligand precursor.



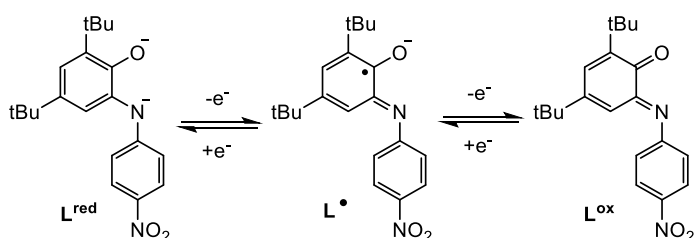
Highlights

- Metal complexes with redox-active non-innocent ligands
- Structurally analogous square-planar complexes of Co, Ni and Cu.
- High near-IR absorption

Keywords

non-innocent ligands / near-IR absorption / metal complexes / redox-active ligands

Ortho-aminophenols and catechols are interesting as redox-active, i.e. non-innocent ligands that can form metal complexes where the formal oxidation state of the metal is uncertain. [1–5] Transition metal complexes of such ligands have attracted attention recently due to their interesting magnetic properties as well as their application in catalysis. [6–9] One example of non-innocent *ortho*-aminophenol derivatives is 2,4-di-*tert*-butyl-6-((4-nitrophenyl)amino)phenol (L, see scheme 1), which is found as an in-situ generated oxidized form in a copper(I) complex $[\text{Cu}(\text{L}^{\text{ox}})(\text{TMPD})]^+$ (TMPD = N,N,N',N'-tetramethylpropylenediamine). [10].



Scheme 1 The different oxidation states of the deprotonated ligand L.

In present study, the ligand L was used to prepare complexes $[\text{ML}^{\bullet}_2]$ ($\text{M} = \text{Ni}, \text{Co}, \text{Cu}$) by the reaction of the ligand precursor H_2L , prepared from 3,5-di-*tert*-butyl catechol and 4-nitroaniline, with metal(II)acetates in 2:1 ratio to yield the respective $[\text{ML}^{\bullet}_2]$ complexes (see Supplementary material for the experimental details). The NMR studies provided little information about the structure of $[\text{CoL}^{\bullet}_2]$ and $[\text{CuL}^{\bullet}_2]$ because of the paramagnetic nature of the complexes. The ^1H -NMR spectrum of the $[\text{NiL}^{\bullet}_2]$ complex, however, displays two distinct singlets (1.10 and 1.03 ppm) at the aliphatic region which are due to the *tert*-butyl groups. In the aromatic region, there are four observable multiplets. The protonation state of the coordinated ligands was also verified using electrospray ionization (ESI-MS) mass spectroscopy. $[\text{CoL}^{\bullet}_2]$ gave interpretable results with both positive and negative ionization modes. Similar m/z ratios, which correspond to $[\text{M}-\text{H}]^+$ and $[\text{M}-\text{H}]^-$, were detected at 738.2954 and 738.2978, respectively. The peak pattern was also typical for a Co compound. For $[\text{NiL}^{\bullet}_2]$, the MS-spectrum gave, only with positive ionization, a distinguishable Ni peak pattern at $m/z = 738.2743$, which corresponds to $[\text{M}]^+$ ion. With both ionization modes, $[\text{M}]^+$ and $[\text{M}]^-$ were detected, along with a typical peak pattern, for $[\text{CuL}^{\bullet}_2]$ at $m/z = 743.2830$ and $m/z = 743.2818$, respectively. This indicates that the complex can lose or gain an electron in the ionization process. The TG measurements showed high thermal stability, the complexes start to decompose under a N_2 atmosphere at *ca.* 340 ($[\text{CoL}^{\bullet}_2]$), 360 ($[\text{NiL}^{\bullet}_2]$) and 260 °C ($[\text{CuL}^{\bullet}_2]$).

Single-crystal X-ray diffraction studies of the intense-colored compounds displayed that all three complexes crystallize in triclinic space group $P\bar{1}$. The Co and Cu complexes are isostructural, with one-half of the complex unit in asymmetric unit and one whole molecule occupies the unit cell. In the crystal structure of $[\text{NiL}^*_2]$, however, there are two halves of a complex in an asymmetric unit and two molecules consists the unit cell. All of the solid state structures reveal the formation of neutral molecular complexes with square planar coordination geometries and completely flat $\cdot\text{L}-\text{M}-\text{L}\cdot$ backbones. Figure 1 illustrates the conformational similarity of the complexes. The close inspection of the interatomic bond parameters shows that the C–C distances in the aminophenol C6-ring are not equidistant but consist of two clearly shorter and four longer C–C bonds (see Table S2). The N7–C6 bonds are shorter than the N7–C8 bonds, whereas the O–C aromatic distances are shorter than what can be expected for a phenolate ligand. The ligands therefore adopt an o-iminobenzosemiquinone configuration with formal charge of -1 . This is in accordance with a previous investigation of analogous copper(II) and nickel(II) complexes by Wieghardt and co-workers[1]. The ligand charge can be further examined by means of metrical oxidation state (MOS), which has been used to estimate the formal oxidation states of coordinated o-aminophenol moieties on the basis of their geometrical parameters.[2] With these complexes, the calculated MOSs for the respective ligands were -1.28 ($[\text{CoL}^*_2]$), -1.10 ($[\text{NiL}^*_2]$) and -0.84 ($[\text{CuL}^*_2]$). These MOS values display a periodical trend of these transition metals in a delocalized system and provide further support to the structural interpretation that these complexes consist of o-iminobenzosemiquinonato(-1) ligands and metals in $+2$ oxidation state. The structure of the bidentate ligand in $[\text{CuL}^*_2]$ can be compared with that in iminoquinone complex $[(\text{TMPD})\text{CuL}^{\text{ox}}]$ (TMPD = *N,N,N',N'*-tetramethylpropylenediamine).[10] The overall structure and bonding parameters of the ligand are very similar in both compounds, although the O1–C1 distance in $[\text{CuL}^*_2]$ is 1.293 \AA , whereas in $[(\text{TMPD})\text{CuL}^{\text{ox}}]$ it is 1.250 \AA . Similarly, the Cu–O1 bonding distance is shorter in $[\text{CuL}^*_2]$ (1.915 \AA) than in $[(\text{TMPD})\text{CuL}^{\text{ox}}]$ (2.164 \AA).

Regarding the molecular packing in the solid state, the complexes form stacking of molecular units into slipped columns along the crystallographic a -axis. The observed intermolecular distances within these columns are rather long – perhaps due to steric hindrance arising from the tert-butyl groups – and thus no strong coupling interactions between the adjacent molecules are expected.

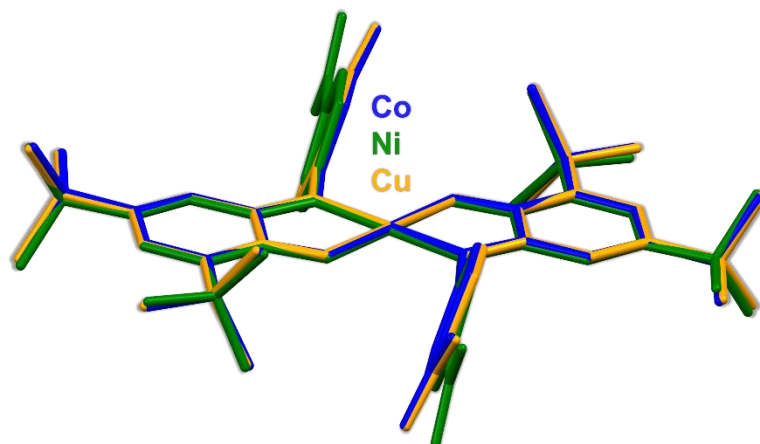


Figure 1 Comparison between the geometries of molecular units in crystal structures of $[ML^*_2]$ [$M = \text{Co}$ (blue), Ni (green) and Cu (yellow)].

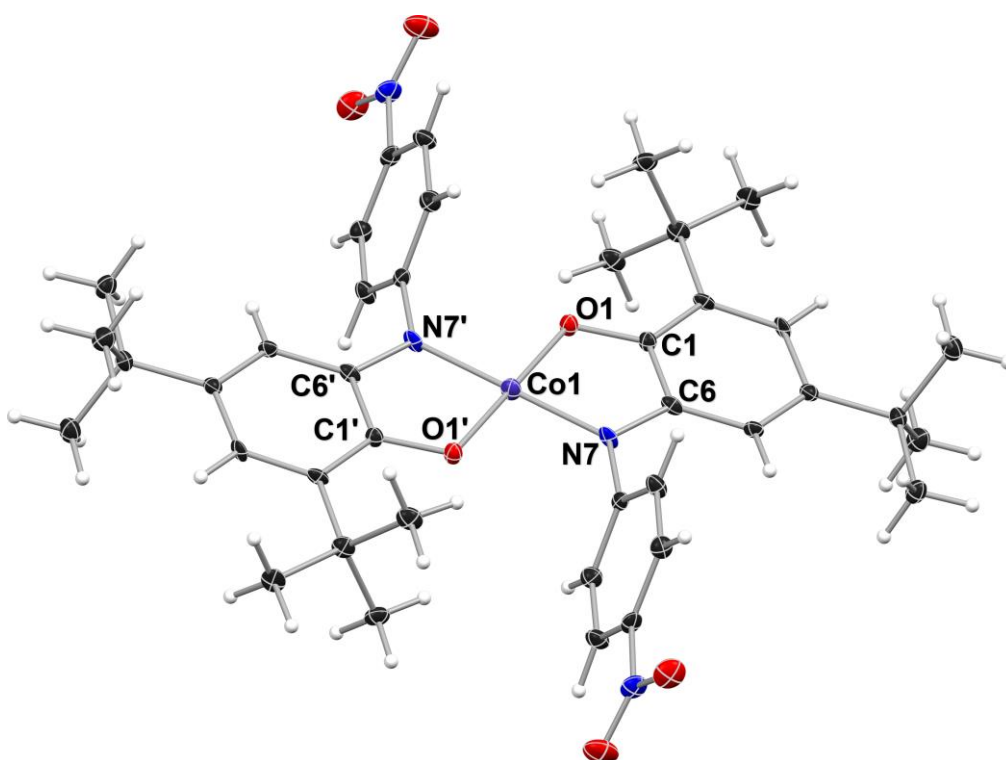


Figure 2 The complex unit in the crystal structure of $[\text{CoL}^*_2]$. Thermal ellipsoids are drawn at the 30% probability level.

Cyclic voltammetry was used to study the redox stability and the characteristic redox behavior of the complexes by running the measurements in the potential range from + 1.5 to – 2.1 V vs Fc^+/Fc . At low potentials, $[\text{CoL}^*_2]$ and $[\text{NiL}^*_2]$ complexes began to decompose. In a narrower potential range, however, the complexes proved to sustain the shape of the cycle. $[\text{CuL}^*_2]$ presented three one electron transfer processes in the cathodic range (-0.98, -0.77 and -0.14 V) and one transfer process (+0.11 V) in the anodic range. These are coherent with similar Cu complexes in the literature[1,11] and they are thus assignable as ligand centered processes. $[\text{CoL}^*_2]$ and $[\text{NiL}^*_2]$ were measured in the range from +1.5 to – 1.1 V vs Fc^+/Fc . There was one transfer process in the anodic range at +0.58 V and one reversible

transfer process at -0.76 V and one irreversible process at -0.42 V in the cathodic range. [NiL[•]₂] presented one irreversible process (-0.43 V) in the cathodic range and one irreversible process (+0.28 V) in the anodic range. The current responses of these electron transfer processes, concerning [CoL[•]₂] and [NiL[•]₂], were low in comparison with the responses of [CuL[•]₂].

The optical absorption properties of the complexes were studied to probe their possible use as dyes in photovoltaics. The UV-vis-NIR –spectra in CH₂Cl₂ present distinct absorption peaks for each complex in the vis/NIR range (Table S3). The absorption coefficients of the different complexes range from modest to significantly high when compared with the coefficient of the standard ruthenium sensitizer dye ($\epsilon \approx 1.4 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$, $\lambda = 538 \text{ nm}$)[12]. The absorption spectra are rather similar in shape both in the solid state and in CH₂Cl₂ solution for all complexes. The X-band EPR spectra of powder samples of [CoL[•]₂] and [CuL[•]₂] were measured at 20 K. [CoL[•]₂] presented an axial EPR spectrum where the g-values were $g_{\parallel} = 2.905$ and $g_{\perp} = 2.020$. These values correspond well[13] to a square-planar d⁷ high-spin Co²⁺ moiety and indicate that the most of the compound's spin density arises from the paramagnetic metal center. The EPR spectrum of [CuL[•]₂] exhibited behavior that is typical for a Cu²⁺ ion containing species albeit rather weak hyperfine coupling was observed. The g-values were $g_{\parallel} = 2.225$ and $g_{\perp} = 2.054$, which are typical for a square-planar Cu²⁺ complex but the lack of hyperfine interaction may signify that although most of the spin density is on the copper ion, some is delocalized on neighboring atoms.

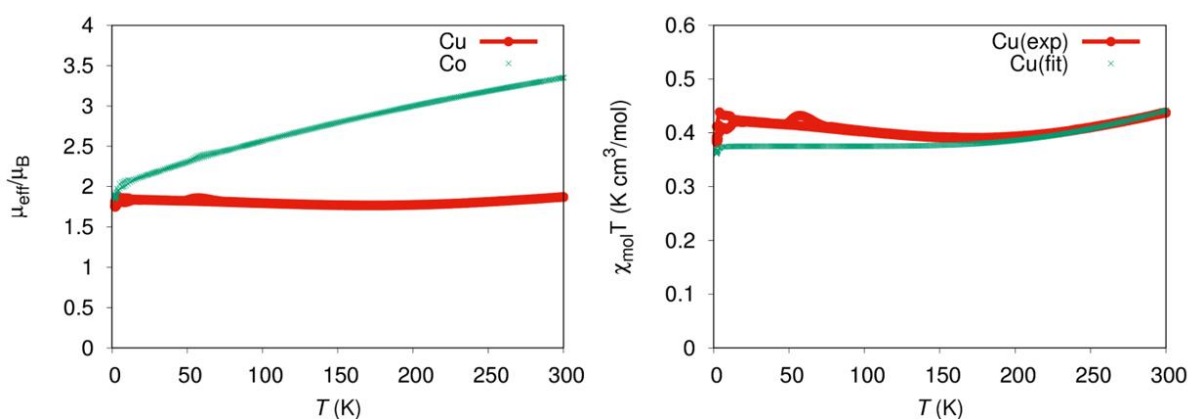


Figure 3 Left: The μ_{eff} vs. T plots for [CoL[•]₂] (upper line) and [CuL[•]₂] (lower line). Right: The experimental (upper line) and fitted (lower line) $\chi_{\text{mol}}T$ vs. T plot for [CuL[•]₂] in cgs units. The bulges seen at *ca.* 60 K, are due to some air in the SQUID instrument. The discrepancy in $\chi_{\text{mol}}T$ vs. T plot at lower temperatures is mostly due to the sample holder.

[CoL[•]₂] and [CuL[•]₂] were studied also with SQUID magnetometer to further investigate the paramagnetic nature of the complexes in the solid state. The field dependence curves measured at 2 K for [CoL[•]₂] and [CuL[•]₂] are typical for paramagnetic complexes (See Figures S16 and S17 in supplementary material). The temperature dependence of the susceptibilities were also measured

whereas the calculated effective magnetic moments would suggest that complexes are consisted from two organic radical ligands and a paramagnetic metal center. For example, $[\text{CuL}^{\bullet}_2]$ has $\mu_{\text{eff}} \approx 1.8 \mu_{\text{B}}$, which equals well with a single unpaired spin on the complex unit (see Figure 3). The obtained $\chi_{\text{mol}}T$ data for $[\text{CuL}^{\bullet}_2]$ was utilized in a computational fitting[14] with the presumption that the complex has two radical entities with a square-planar Cu(II) metal center and possible *g*-values ranging from 2.00 to 2.30. Figure 3 show the μ_{eff} vs. *T* plots for bot metal complex as well as the $\chi_{\text{mol}}T$ vs. *T* plot for the Cu(II) complex. The experimental $\chi_{\text{mol}}T$ vs. *T* plot as well as the simulation resembles the results obtained previously for related complexes [15]. Therefore, we may conclude that the spin system of $[\text{CuL}^{\bullet}_2]$ can be represented as $(\uparrow\uparrow\downarrow)$, *i.e.* the radical-radical coupling is antiferromagnetic while the unpaired electron is located on the metal center. The essence of the spin states of $[\text{CoL}^{\bullet}_2]$ is rather vexatious to clarify due to zero-field splitting (ZFS).

Finally, some photovoltaic performance of the molecules was tested as dye sensitizers in conventional sealed dye-sensitized solar cells prepared on glass substrates[16]. However, the devices that were fabricated, failed to produce any electric current in the vis-NIR range (see Supplementary material).

In conclusion, three structurally analogous square planar transition metal complexes were synthesized and characterized. The complexes were highly stable in ambient conditions and they exhibited strong absorptions in the NIR range as well. As expected, the Co(II) and Cu(II) complexes were paramagnetic, whereas the Ni complex shows diamagnetic properties typical for a square planar low-spin Ni(II) center.

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