Electronic Perturbation in a Molecular Nanowire of [IrCl₅(NO)]⁻ Units

Florencia Di Salvo, Natalia Escola, Damián A. Scherlis, Darío A. Estrin, Carlos Bondía, Daniel Murgida, José M. Ramallo-López, Félix G. Requejo, Linda Shimon, and Fabio Doctorovich

Abstract: The nitrosyl in [IrCl₅(NO)]⁻ is probably the most electrophilic known to date. This fact is reflected by its extremely high IR frequency in the solid state, electrochemical behavior, and remarkable reactivity in solution. PPh₄[IrCl₅(NO)] forms a crystal in which the [IrCl₅(NO)]⁻ anions are in a curious wire-like linear arrangement, in which the distance between the N–O moiety of one anion and the trans chloride of the upper one nearby is only 2.8 Å. For the same complex [IrCl₅(NO)]⁻ but with a different counterion, Na[IrCl₅(NO)], the anions are stacked one over the other in a side-by-side arrangement. In this case the electronic distribution can be depicted as the closed-shell electronic structure IrV(NO)⁺, as expected for any d⁶ third-row transition metal complex. However, in PPh₄[IrCl₅(NO)] an unprecedented electronic perturbation takes place, probably due to NO–Cl acceptor–donor interactions among a large number of [IrCl₅(NO)]⁻ units, favoring a different electronic distribution, namely the open-shell electronic structure IrIV(NO). This conclusion is based on XANES experimental evidence, which demonstrates that the formal oxidation state for iridium in PPh₄[IrCl₅(NO)] is +4, as compared with +3 in K[IrCl₅(NO)]. In agreement, solid-state DFT calculations show that the ground state for [IrCl₅(NO)]⁻ in the PPh₄⁺ salt comprises an open-shell singlet with an electronic structure which encompasses half of the spin density mainly localized on a metal-centered orbital, and the other half on an NO-based orbital. The electronic perturbation could be seen as an electron promotion from a metal–chloride to a metal–NO orbital, due to the small HOMO–LUMO gap in PPh₄[IrCl₅(NO)]. This is probably induced by electrostatic interactions acting as a result of the closeness and wire-like spatial arrangement of the Ir metal centers, imposed by lattice forces due to π–π stacking interactions among the phenyl rings in PPh₄⁺. Experimental and theoretical data indicate that in PPh₄[IrCl₅(NO)] the Ir–N–O moiety is partially bent and tilted.

Keywords: electron transfer · iridium · nanostructures · nitrosyl · valence isomerization

Introduction

Metal nitrosyls have attracted considerable attention since the discovery of endogenous NO as a biomolecule.[1] The nitrosyl in K[IrCl₅(NO)] is probably the most electrophilic electron-poor nitrosyl (“NO⁺”) known to date. This fact is reflected by its extremely high IR frequency in the solid state (2006 cm⁻¹),[2] electrochemical behavior,[3,4] and reactivity.[5] In particular, the electronic perturbation in PPh₄[IrCl₅(NO)] is unprecedented.

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markable reactivity\cite{5,6} observed in solution. According to the formalism of Enemark and Feltham,\cite{7} the crystal structure of this hexacoordinated [MNO]\textsuperscript{6} comprises an octahedral anion with a practically linear Ir–NO moiety (Ir-N-O 174.3°).\cite{8}

Third-row transition metal complexes with an even number of electrons generally have a low-spin electronic distribution in the ground state, where each electron pair occupies just one orbital. This is mainly because of the considerable energy gap between the HOMO and the LUMO and the relatively low electronic repulsion. Spin crossover, a temperature-dependent low-spin to high-spin transition, is well known for first-row transition metals, especially iron,\cite{9} but very rare for second- or third-row transition metals.

Intramolecular electron transfer involving a metal ion and a redox-active ligand can give two different electronic isomers (more specifically, valence tautomers).\cite{10} It can be induced not only by temperature variations but also by irradiation or pressure, or other changes in the environment such as counterion changes.\cite{11} This interconversion and the spin crossover mentioned above can be considered as entropy-driven processes. Most of the reported examples which exhibit valence tautomeration are based on quinone or quinone-type ligands with a series of transition metal ions such as Co, Cu, Ni, and Mn, and more recently Fe. No examples showing electronic transfer or promotion involving either a third-row metal such as iridium or an NO ligand have been reported yet.

Based on solid-state and in-vacuo DFT calculations, XANES, FTIR, and Raman experimental evidence, two different electronic distributions can be observed for the same anion, [IrCl\textsubscript{5}(NO)]\textsuperscript{−} for Na\textsuperscript{+} and K\textsuperscript{+} salts; and Ir\textsuperscript{3+}–NO\textsuperscript{−} for PPh\textsubscript{4}\textsuperscript{+} and AsPh\textsubscript{4}\textsuperscript{+} ones.\cite{12} In the second case, π–π stacking interactions among the phenyl rings could be the motive forces producing an electronic promotion from a metal-based orbital to an NO-based orbital due to a decrease in the HOMO–LUMO gap in the solid.

### Results and Discussion

As expected, the crystal structure of Na[IrCl\textsubscript{5}(NO)] obtained by our group (Figure 1 and Supporting Information) is almost coincident with the structure of K[IrCl\textsubscript{5}(NO)] mentioned above and with the DFT-optimized structure of the isolated ion (Table 1). The anions are stacked one over the other in a side-by-side arrangement (Figure 2A).

However, PPh\textsubscript{4}[IrCl\textsubscript{5}(NO)] and AsPh\textsubscript{4}[IrCl\textsubscript{5}(NO)], both octahedral, have a rather different crystal structure (Figure 2B and Supporting Information). Their crystal lattices have two interesting features: the phenyl rings are perfectly stacked one over the other, determining the lattice structure; and the anions are placed in a perfectly linear arrangement, reminiscent of an infinite “wire.” This wire could be considered as a molecular nanowire embedded in a matrix of PPh\textsubscript{4}\textsuperscript{+} (or AsPh\textsubscript{4}\textsuperscript{+}) counterions, leaving the “hole” occupied by the anions. Nanowires are anisotropic nanocrystals with large aspect ratios (length/diameter),\cite{13} while molecular nanowires are wires composed of repeating molecular units, either inorganic or organic.\cite{14} Nevertheless, the peculiar wire-like arrangement and the short NO\textsuperscript{−}–Cl\textsuperscript{−} distance between the N–O moieties of one anion and the trans chloride of the nearby one above (2.8 Å) observed in the case of PPh\textsubscript{4}[IrCl\textsubscript{5}(NO)], as compared with its Na\textsuperscript{+} and K\textsuperscript{+} counter-
The diamagnetism of PPh₄⁺ represented by Ir⁴⁺ fore investigated the possibility of an electronic distribution unusual. We therefore suggested that the electronic distribution for this third-row transition metal complex was unusual. The electronic distribution for [IrCl₅(NO)] was provided by X-ray absorption near-edge structure (XANES) measurements in the solid state at the L₃ edge (Figure 3). The L₃ absorption edge of transition metals has important features which can reveal the occupancy of d states. For instance, third-row transition metals exhibit a large peak after the absorption edge, usual- ly called a “white line”. The white line intensity is directly related to the density of unoccupied states. In particular, the Ir L₃-edge XANES spectrum is characterized by this white line, which corresponds primarily to the electric dipole allowed electronic transitions from 2p states to 5d ones. For the third-row transition metals it has been shown that the position of the absorption edge and the intensity of the occurrence in the solid state? As mentioned above, π–π stacking interactions among the phenyl rings are very probably taking place, since the Ir–Ir distance between two anions is less than the minimum required for stable linear nitrosyls (see below). In the case of benzene, the π–π stacking energy of interaction could be around 2–4 kcal mol⁻¹. [15, 16] Since in the case of the phosphonium complex there are four rings per anion, 8–16 kcal mol⁻¹ would be the approximate energy of the π–π stacking interactions, which is in the range of the energy difference between the OSS (open-shell singlet) and the CSS for the isolated anion in vacuo (≈14 kcal mol⁻¹; see Supporting Information).

Strong experimental evidence supporting the Ir⁵⁺–NO’ configuration in PPh₄[IrCl₅(NO)] was provided by X-ray absorption near-edge structure (XANES) measurements in the solid state at the L₃ edge (Figure 3). The L₃ absorption edge of transition metals has important features which can reveal the occupancy of d states. For instance, third-row transition metals exhibit a large peak after the absorption edge, usually called a “white line”. The white line intensity is directly related to the density of unoccupied states. In particular, the Ir L₃-edge XANES spectrum is characterized by this white line, which corresponds primarily to the electric dipole allowed electronic transitions from 2p states to 5d ones. For the third-row transition metals it has been shown that the position of the absorption edge and the intensity of the

![Figure 1. Anion portion of the Na[IrCl₅(NO)] X-ray crystal structure. Thermal ellipsoids are drawn at the 50% level.](image1)

Table 1. FTIR NO stretching frequencies and selected structural parameters for [IrCl₅(NO)]⁻ and related species.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ν(NO) [cm⁻¹]</th>
<th>θ MNO [°]</th>
<th>d(O–N) [Å]</th>
<th>d(N–N) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>K[IrCl₅(NO)]</td>
<td>2006</td>
<td>174.3</td>
<td>1.124</td>
<td>1.760</td>
</tr>
<tr>
<td>Na[IrCl₅(NO)]</td>
<td>1986</td>
<td>172.9</td>
<td>1.140</td>
<td>1.760</td>
</tr>
<tr>
<td>PPh₄[IrCl₅(NO)] (tilted)</td>
<td>1952</td>
<td>166.9</td>
<td>1.176</td>
<td>1.776</td>
</tr>
<tr>
<td>[IrCl₅(NO)]⁻</td>
<td>1946</td>
<td>179.2</td>
<td>1.158</td>
<td>1.750</td>
</tr>
<tr>
<td></td>
<td>2027</td>
<td>178.9</td>
<td>1.140</td>
<td>1.764</td>
</tr>
<tr>
<td>[IrCl₆(NO)]⁺</td>
<td>1650</td>
<td>139.9</td>
<td>1.190</td>
<td>1.860</td>
</tr>
<tr>
<td>K[Br₆(NO)]⁺</td>
<td>1755</td>
<td>141.1</td>
<td>1.180</td>
<td>1.873</td>
</tr>
<tr>
<td>Na₃[Fe(CN)₅(NO)]⁻</td>
<td>1944</td>
<td>175.7</td>
<td>1.124</td>
<td>1.653</td>
</tr>
<tr>
<td>Na₃[Ru(CN)₅(NO)]⁻</td>
<td>1926</td>
<td>173.9</td>
<td>1.127</td>
<td>1.776</td>
</tr>
</tbody>
</table>

[a] Experimental data from KBr pellet, and X-ray crystallography. [b] Experimental data from KBr pellet. [c] DFT optimization in the solid state (see below). [d] EXAFS data (see below). [e] DFT optimized structure in vacuo, DZPV basis sets for N, O and Cl, LANL2DZ basis sets and pseudopotential for Ir; BPW91 functional for the first line and B3LYP for the second one. [f] Ref. [8]. [g] Ref. [4].

parts, suggested that the electronic distribution for this third-row transition metal complex was unusual. We therefore investigated the possibility of an electronic distribution represented by Ir⁵⁺–NO’ for the PPh₄⁺ complex, instead of Ir⁵⁺–NO⁺ (as for the K⁺ and Na⁺ ones). In principle, the lone electron on NO’ could be paired or unpaired with the metal-based lone electron, forming a singlet or a triplet species respectively. This electronic isomerism could be viewed as produced by packing forces in the crystal, which would be very rare for second- or third-row transition metals. The possibility of a triplet (Ir↑–NO↑) was discarded because of the diamagnetism of PPh₄[IrCl₅(NO)], as observed by EPR and SQUID measurements (Supporting Information). Therefore, the expected situation was a singlet species (Ir↓–NO↓) with a low-spin Ir⁵⁺ center (S = ±1/2) coupled antiferromagnetically to NO’ (S = ±1/2). In the gas phase, a nitrosyl complex in an open-shell state (triplet or singlet) is less stable than the linear CSS (closed-shell singlet) (Supporting Information). Why, then, would the electronic perturbation occur in the solid state? As mentioned above, π–π stacking interactions among the phenyl rings are very probably taking place, since the Ir–Ir distance between two anions is less than the minimum required for stable linear nitrosyls (see below). In the case of benzene, the π–π stacking energy of interaction could be around 2–4 kcal mol⁻¹. [15, 16] Since in the case of the phosphonium complex there are four rings per anion, 8–16 kcal mol⁻¹ would be the approximate energy of the π–π stacking interactions, which is in the range of the energy difference between the OSS (open-shell singlet) and the CSS for the isolated anion in vacuo (≈14 kcal mol⁻¹; see Supporting Information).

Strong experimental evidence supporting the Ir⁵⁺–NO’ configuration in PPh₄[IrCl₅(NO)] was provided by X-ray absorption near-edge structure (XANES) measurements in the solid state at the L₃ edge (Figure 3). The L₃ absorption edge of transition metals has important features which can reveal the occupancy of d states. For instance, third-row transition metals exhibit a large peak after the absorption edge, usually called a “white line”. The white line intensity is directly related to the density of unoccupied states. In particular, the Ir L₃-edge XANES spectrum is characterized by this white line, which corresponds primarily to the electric dipole allowed electronic transitions from 2p states to 5d ones. For the third-row transition metals it has been shown that the position of the absorption edge and the intensity of the
white line at the L\textsubscript{3} edge are both directly related to the oxidation number of the absorbing atom.\cite{17} The higher the oxidation state of the metal, the more positive the overall charge of the atom; then more energy is required to excite an electron out of an orbital.\cite{18} Besides, as the oxidation number of the absorbing atom increases, the edge moves to higher energy and the intensity of the white line increases because of the higher density of empty states. For both energy shifts and white-line intensity variations, XANES becomes an ideal tool for the determination of changes in the oxidation state of metals.\cite{18,19} Sometimes the variation in the oxidation state results in a smaller energy shift than the intrinsic energy uncertainty at the corresponding electronic level, so this methodology is not sensitive enough to determine the energy shift and the only parameter suitable for determination of the oxidation state is the intensity of the white line. Moreover, when the nature of the moieties surrounding the absorbing atoms differs among samples, the shift is not an unequivocal parameter since the total energy shift comprises an intricate superposition of factors (for example, geometry, orbital hybridization, charge transfer).\cite{20}

Like the L\textsubscript{3} white lines, the L\textsubscript{2} white lines for Ir are attributed to transitions from 2p orbitals to partially occupied bands at the Fermi level with a largely 5d character. Since precisely d electrons are involved in Ir–Cl or Ir–N bonds, the L\textsubscript{2} and L\textsubscript{3}-edge XANES spectra will be particularly sensitive to changes in redox state. L\textsubscript{2} and L\textsubscript{3} are associated with the dipole allowed electronic transitions 2p\textsubscript{1/2}→5d\textsubscript{5/2} and 2p\textsubscript{3/2}→5d\textsubscript{3/2} respectively, but the increment at the L\textsubscript{3} white line does not necessarily imply that L\textsubscript{2} should also increase, because the overlapping differs at the 5d\textsubscript{5/2} and 5d\textsubscript{3/2} levels of Ir in the molecule. Moreover, the constant intensity of the L\textsubscript{2} white line indicates that the increment originates mainly in variations in the occupancy at the 5d\textsubscript{5/2} level. It is interesting that the XANES spectra at the L\textsubscript{2} edge are exactly the same for PPh\textsubscript{4}[IrCl\textsubscript{5}(NO)] and K[IrCl\textsubscript{5}(NO)] (see Supporting Information), demonstrating that the results observed at the L\textsubscript{3} edge do not correspond to experimental artifacts such as thickness effects or inhomogeneities in the sample.\cite{21}

The area of the absorption peak in Figure 3 at around 11.22 keV for PPh\textsubscript{4}[IrCl\textsubscript{5}(NO)] is notably larger than that for K[IrCl\textsubscript{5}(NO)], indicating a higher density of unoccupied states for the Ir center: that is, a higher oxidation state for Ir in PPh\textsubscript{4}[IrCl\textsubscript{5}(NO)]. The expected energy shift is not observable for the two different samples because the resolution of the energy measurements (approximately 5 eV) is not great enough for the small differences expected (ca 1 eV) to be detected.

In the particular case of Ir L edges, the increment in the Ir L\textsubscript{2} white-line intensity with its oxidation state was verified by XANES measurements for three different Ir reference compounds with similar close surroundings but different oxidation states (references: Ir\textsuperscript{IV}L\textsubscript{6}, K\textsubscript{2}[IrCl\textsubscript{6}]; Ir\textsuperscript{III}L\textsubscript{6}, K\textsubscript{2}[IrCl\textsubscript{6}]; Ir\textsuperscript{II}L\textsubscript{2}Cl\textsubscript{2}, Ir\textsubscript{2}(C\textsubscript{8}H\textsubscript{12})\textsubscript{2}Cl\textsubscript{2}). To compare the two sets of compounds, the white-line area was determined and plotted versus the oxidation state for the references, giving an approximately linear relationship. Under this approximation, from the white-line area of K[IrCl\textsubscript{5}(NO)] and PPh\textsubscript{4}[IrCl\textsubscript{5}(NO)] the oxidation state for the latter was determined as 3.9, that is, 0.9 units higher than for the K[IrCl\textsubscript{5}(NO)] sample (see Figure 4).

To provide more evidence for the OSS configuration, DFT calculations were performed both in vacuo on the isolated anion [IrCl\textsubscript{5}(NO)]\textsuperscript{−}, and in the solid state on the extended, infinitely repeated crystallographic structure of PPh\textsubscript{4}[IrCl\textsubscript{5}(NO)]. In agreement with the XANES results, the total and absolute magnetization in the solid (single-crystal X-ray geometry), computed as \(\int(|\rho\cdot\rho|)\,d\tau\) and \(\int(|\rho\cdot\rho|)\,d\tau\) respectively, were 0.0 and 4.0 \(\mu\text{B}\), consistent with an OSS (Supporting Information). An absolute magnetization of 2.0 \(\mu\text{B}\) is indicative of open-shell systems with two unpaired electrons; in this case a value of 4.0 originates in two metallic centers per unit cell. The same results were obtained for a DFT partially optimized structure in the solid state (see below), although in this case the OSS is 8.7 kcalmol\textsuperscript{−1} more stable than the experimental X-ray crystal structure. Figure 5 displays the total spin density as obtained from the solid-state calculations, showing half of the spin density localized on a metal-centered orbital and slightly spread onto the equatorial chlorides, and the other half localized on an
of the OSS, probably because of electrostatic interactions. The wire-like arrangement are responsible for the stabilization that the proximity of the anions and their singular nano-state is represented by the CSS. It is evident from the above Figure 6 are located 21.3/P3X apart instead of 7.8 3/P3X, the ground state of the counterions. The likelihood of an electronic transition taking place during the X-ray measurements was also discarded since the IR spectra obtained in vacuo do not account for the dispersive forces arising between aromatic rings, we do not expect this flaw to produce any relevant effect on the NO geometry or the spin density, since all atoms involved in π–π stacking were frozen in their experiment coordinates during the calculations.

As an electron transfer or another type of electronic influence could take place from the phosphonium counterions to [IrCl(NO)]−, calculations in the solid state were also performed by removing the counterions from the crystal cell, leaving isolated molecular nanowires. In this case also, an OSS was obtained as the ground state (Figure 6), indicating that there are no important electronic effects derived from the presence of the counterions. The likelihood of an electronic transition taking place during the X-ray measurements was also discarded since the IR spectra obtained immediately after irradiation appeared no different from that corresponding to the starting material, and no color changes were observed during or after irradiation.

It is striking that when the Ir centers of the structure in Figure 6 are located 21 Å apart instead of 7.8 Å, the ground state is represented by the CSS. It is evident from the above that the proximity of the anions and their singular “nanowire-like” arrangement are responsible for the stabilization of the OSS, probably because of electrostatic interactions.

A possible explanation for the open-shell configuration is provided by inspecting the frontier orbitals in [IrCl(NO)]− dimers and trimers. Consistently with this, DFT in vacuo calculations show that the degeneracy of the orbitals corresponding to the isolated anions is broken for dimers and trimers with Ir–Ir distances constrained to the value observed for the crystal structure (7.807 Å). The energy gap between the HOMO and the LUMO (∆E_{H-L}) for each of the systems, calculated by DFT in vacuo, decreases considerably for trimers and trimers. For example, in the case of the in-vacuo optimized geometry: ∆E_{H-L} = 1.31, 0.70, and 0.40 eV for the monomer, dimer, and trimer, respectively (taking the last two as whole units). For a trimer with d_{Ir-Ir} = 21 and 31 Å, ∆E_{H-L} = 1.00 and 1.14 eV, respectively. These results point toward the formation of a conducting band by strong interactions between the anions.

Raman spectra of the two types of crystals provide further support for the results above. For K[IrCl(NO)] the NO stretching mode (ν_{NO}) is observed at 1976 cm−1 with very low intensity, while in AsPh 4[IrCl(NO)] (which behaves analogously to the PPh 4+ salt and has a crystal structure very similar to that of PPh 4[IrCl(NO)]), this band gains intensity and shifts down to 1955 cm−1 (Figure 7 and Supporting Information). IR spectra show intense bands at 1906 cm−1 for K[IrCl(NO)] and 1952 cm−1 for AsPh 4[IrCl(NO)] and PPh 4[IrCl(NO)].

Nitrosyl-based reduction, M=NO+ → M=NO−, causes a large downshift (≈300 cm−1) of the νNO band, as well as an increase in the Raman compared with the IR activity. On the other hand, metal-based oxidation, MIII=NO→MIV=NO+, shifts the νNO band in the opposite direction due to diminished backbonding. This shift is expected to be smaller than for nitrosyl reduction, as observed experimentally for different MNO moieties. Thus, the net effect for an IRIII−NO→IPV−NO transition is expected to be a relatively small downshift of the νNO band, as observed in the present work.

The weak Raman band observed at 556 cm−1 for K[IrCl(NO)] is assigned tentatively to Ir-N-O bending (δ_{IrNO})
Figure 7. Single-crystal Raman spectra recorded with 514 nm excitation at 83 K. A) K[IrCl₅(NO)]; B) AsPh₄[IrCl₅(NO)]. The intensities are normalized by the strongest low-frequency band for a better comparison.

although some degree of mixing with νIr–N modes cannot be ruled out.[24] For AsPh₄[IrCl₅(NO)] crystals, this band gains intensity and shifts to higher energy, 573 cm⁻¹. Both the increased intensity and the higher frequency are indicative of a tilted IrVIl–NO’ moiety in the latter crystals.[25]

**Geometry of the Ir–N–O moiety:** When DFT in-vacuo calculations were performed for [IrCl₅(NO)]⁻ dimers and trimers (Figure 8) with Ir–Ir distances constrained to the value observed for the crystal structure (7.807 Å) and the arrangement corresponding to the phosphonium compound, some bending and tilting for Ir-N-O was observed, indicating that packing forces (probably π−π stacking between the phenyl rings) could be operating in the crystal. Similar results were observed when the optimization of one [IrCl₅(NO)]⁻ unit was performed in a background of NPA-calculated charges (NPA, natural population analysis) corresponding to two [IrCl₅(NO)]⁻ units and 12 counterions, all of them located as in the X-ray PPh₄⁺ structure (see Supporting Information). The interactions mentioned above seem to be producing an

Ir–Ir distance constraint, which becomes too short to accommodate anions with a linear Ir-N-O moiety. In the similar case of (AsPh₄)₂[Fe(CN)₅NO], where again the cations determine the lattice structure and leave little space for the anions,[25,26] the anions’ preferred position is in a tilted orientation instead of just the M–N–O moiety being bent or tilted. Therefore, in the case of PPh₄[IrCl₅(NO)], an interaction between the trans chloride of one anion and the NO of the anion below it could be taking place, helping to form the “wire” mentioned above (the Cl–O distance is 2.8 Å).

Although the X-ray measurements in the case of PPh₄[IrCl₅(NO)] were of excellent quality and the structure was perfectly defined for the counterions and all the Ir–Cl bonds, due to crystal disorder some uncertainty remained regarding the structure of the Ir-N-O moiety. Refinements were performed with anisotropic or isotropic parameters (see Supporting Information; an almost equal structure was obtained for AsPh₄[IrCl₅(NO)]). In all cases a large ellipsoid was observed surrounding the N atom, suggesting that it is probably located slightly off-axis. However, crystal disorder—which gives rise to four different N atom orientations—and the presence nearby of the heavy Ir atom prevent establishment of the exact position of the N atom. The distance between its four different orientations are close to the resolution of the instrumental. While under the experimental conditions of our measurements the maximum achievable instrumental resolution is approximately 0.4 Å, the distance between the N atom positions according to the DFT optimizations in the solid state (see below) would be 0.43 Å.

DFT solid-state calculations were performed on the crystal structure in periodic boundary conditions, relaxing the spatial coordinates of the N and O atoms while freezing the rest of the coordinates at the experimental X-ray positions. The use of DFT to complement X-ray results when structural disorders blur the crystallographic parameters is now a common practice, often applied to elucidate the bonding mode of diatomic ligands such as NO or CO in different transition metal complexes (see, for example, refs. [27] and [28]). The optimized Ir–N and N–O distances are consistent with the X-ray data, with the N–O moiety exhibiting a 7° tilt and a concomitant increase in the Ir-N-O angle. A visual comparison with the single-crystal X-ray geometry shows that the N and O atoms of the optimized structure are within the boundaries of the thermal ellipsoids corresponding to the X-ray refinement (Figure 9).

To determine the Ir near-neighbor environment, X-ray absorption fine structure (EXAFS) measurements were performed for K[IrCl₅NO] and PPh₄[IrCl₅(NO)] (Figure 10 and Supporting Information). EXAFS spectroscopy refers to the oscillatory structure in the X-ray absorption coefficient beyond a 50 eV threshold. The fit of this oscillation gives information about the surroundings of the absorbing atom. In particular, the type, number, and bond lengths of the atoms around the absorbing atom can be obtained. EXAFS analysis is not limited to first neighbors, and distance determinations are now often comparable in accuracy with those from
X-ray diffraction measurements. In addition, a multiple scattering analysis of the EXAFS spectrum can determine atom configuration where three atoms are aligned or almost aligned, because of the shadowing or focusing effect.

Simulations for different geometries for PPh$_4$[IrCl$_5$(NO)] were made using the FEFF6 code. The small peak at about 2.5 Å in Figure 10 is due to both simple scattering from oxygen atoms and multiple scattering paths for Ir-N-O and could be reproduced only by the simulation of structural arrangements where these three atoms were almost aligned. These conditions were met for an Ir-N-O angle greater than 160°. Therefore, a poor fit was obtained when the X-ray crystal structure was used as data input (the Ir-N-O angle in this case is 149°). However, the geometry corresponding to the DFT optimization in the solid state previously described (see Supporting Information, and Figures 5 and 6) gave an excellent fit.

Compared with other [MNO]$^+$ complexes with similar structural characteristics (Table 1), specifically N-O distances and M-N-O angles, the IR stretching frequency for NO in PPh$_4$[IrCl$_5$(NO)] falls in the same frequency region, around 1590 cm$^{-1}$. As expected when an “extra” electron is located in an NO antibonding orbital, the N–O distance is augmented, and its value is between the N–O distances for K[IrCl$_5$(NO)] or Na[IrCl$_5$(NO)] and that calculated for [IrCl$_5$(NO)]$^-$ (Table 1). The correlation of the N–O distance with $\nu_{\text{NO}}$ is excellent (Supporting Information). Moreover, a normal-mode analysis shows that $d_{\text{NO}}$ should be around 1.17 Å for the observed $\nu_{\text{NO}}$ stretching frequency.

In summary, we consider that the DFT optimization in the solid state provides the more accurate structural parameter set for the Ir-N-O moiety, while EXAFS provides excellent parameters for $d_{\text{Ir–N}}$, $d_{\text{Ir–O}}$, $d_{\text{Ir–Cl(eq)}}$ and $d_{\text{Ir–Cl(trans)}}$. These last two distances and $d_{\text{Ir–O}}$ are also provided accurately by the X-ray determination. A selected set of parameters, which gives a reasonably accurate geometry for the Ir-N-O moiety of PPh$_4$[IrCl$_5$(NO)], is that shown in Table 1. However, regardless of the exact value for the Ir-N-O angle and the N–O distance, it is clear that the nitrosyl shows a partially bent/tilted conformation and that a linear N–O does not fit due to the constraint imposed by the short Ir–Ir distance in the “wire-like” arrangement. This peculiar arrangement is probably responsible for the electronic perturbation.

**Conclusion**

The distribution of electrons in Ir$^{III}$–NO$^+$ versus Ir$^{IV}$–NO$^-$ in the case of [IrCl$_5$(NO)]$^-$ can be viewed as an electron promotion from a metal–chloride to a metal–NO orbital due to a decrease in the HOMO–LUMO gap of PPh$_4$[IrCl$_5$(NO)] in the solid state. This is induced by electrostatic interactions acting as a result of the closeness and “wire-like” spatial distribution of the Ir metal centers. This singular arrangement is imposed by lattice forces produced by π–π stacking interactions between the phenyl rings in PPh$_4^+$.

Our theoretical and experimental evidence suggests that this is an interesting case of electronic perturbation in a third-row transition metal complex in the ground state giving rise to valence tautomerism. The high sensitivity of the M-N-O moiety toward the environment, its high electrophilicity, and its interaction with the nearby chloride ligand in this singular “wire-like” [IrCl$_5$(NO)]$^-$ arrangement seems to be the motive force for the unique structural end electronic behavior of pentachloronitrosyliridate, going beyond the original [MNO]$^+$ formalism proposed by Enemark and Feltham and which predicts that isolated [IrNO]$^+$ units should be linear.

**Experimental Section**

**General procedures:** All experimental manipulations were performed under anaerobic and anhydrous conditions using standard Schlenk procedures and a dry box. K[IrCl$_5$(NO)] was purchased from Strem and purified by recrystallization from CH$_3$CN. Na[IrCl$_5$(NO)] was prepared by addition of a 10-fold excess of NaCl to a HCl (1 M) solution of the potassium salt. The solution volume was reduced in a rotary evaporator and
the supernatant kept in a refrigerator for three days. One HCl molecule per Na[IrCl(NO)] unit was observed in the X-ray crystal structure. Tetraphenylphosphonium pentachloronitrosyliridate, PPh₄[IrCl(NO)], was obtained by slowly adding a concentrated solution of tetraphenylphosphonium bromide (0.50m in CH₂CN) to a solution of K[IrCl(NO)] (0.09m in CH₂CN) and washing the precipitate three times with deionized distilled water. The dry, light brown crystals were dissolved in warm CH₂CN (60°C) and this solution was allowed to reach room temperature very slowly. The resulting crystals were suitable for X-ray analysis. An identical technique was employed to obtain the tetraphenylarsonium analogue.

**Instrumental procedures:** UV/Vis spectra were recorded using a Hewlett Packard 8453 diode array spectrometer with quartz cuvettes (10 mm optical path).

IR spectra were recorded using a Nicolet Avatar 320 FTIR spectrometer with either KBr pellets or a Spectra Tech cell for liquids with CaF₂ (Z = 3 cm) windows and a 0.1 mm Teflon spacer. Cyclic voltammetry in aqueous solutions was carried out at a 100 mVs⁻¹ scan rate using a three-electrode configuration (glassy carbon working electrode, Pt counter-electrode, Ag/AgCl reference) and a Te-03 potentiostat and function generator.

For resonance Raman measurements, crystals were placed in a cooling/heating microscope stage (Linkam THMS 600) to vary the temperature between -190 and 200°C with a precision of ±0.1°C. Raman spectra were recorded in backscattering configuration using a confocal microscope attached to a single-stage spectrograph (XY-Jobin Yvon) equipped with a 1800 lines mm⁻¹ grating and liquid nitrogen cooled, back-illuminated charge-coupled device (CCD) detector. The spectral resolution was approximately 2 cm⁻¹ and the increment per data point was 0.47 cm⁻¹. Elastic scattering was removed with a super notch filter (Kaiser). Measurements were performed under liquid N₂ atmosphere. The field modulation frequency was 10–30 s⁻¹. The values reported for each temperature are the average of three scans. The field modulation frequency was varied in the range of 1132/1132, 1005 reflections with 20°C, Θ₀ = 0.0450. Refinement based on F², number of reflections/parameters = 1132/55, R = 0.0333 (based on F² > 2σ(F²)). aR(F) = 0.0991, S = 1.116, (Δ/σ)max = 0.011, Δρmax = 2.081 e Å⁻³, Δρmin = -1.734 e Å⁻³.

**Crystal and collection data and refinement for Na[IrCl(NO)]·HCl:**

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>V (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>monoclinic</td>
<td>P2₁</td>
<td>8.109</td>
<td>8.499</td>
<td>13.236</td>
<td>92.19</td>
<td>90.00</td>
<td>93.42</td>
<td>1132/55</td>
</tr>
</tbody>
</table>

The EPR spectra were recorded at (25.1 ± 1)°C and 9.8 GHz (X band) in an ER-200 spectrometer (Bruker Analytische Messtechnik GmbH, Karlsruhe, Germany). The samples were placed in glass capillaries (1 mm i.d.), sealed at both ends, and housed in 4 mm quartz tubes containing silicone oil to maintain temperature uniformity. The field modulation frequency was 100 kHz, and its amplitude was well below 30% of the minor linewidths in each case, to avoid spectral shape distortions. For the X-ray diffraction studies, data were collected in a Nonius Kappa CCD diffractometer, MoKα radiation (λ = 0.71073 Å), with a graphite monochromator, F = 12002 K. The data were processed with Denzo-Scapack and the refined structure was solved by the Patterson method with SHELXS with full-matrix least-squares refinement based on F² with SHELXL-97. H atoms were treated by a mixture of independent and constrained refinement. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crystals@fiz-karlsruhe.de) on quoting the depository numbers CSD-416353 (Na[IrCl(NO)]·HCl), CSD-417400 (PPh₄[IrCl(NO)]), and CSD-417399 (AsPh₄[IrCl(NO)]).

**Crystal and collection data and refinement for Na[IrCl(NO)]·HCl:**

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**Computational methodology:**

All gas-phase DFT calculations were performed by using the Gaussian 98 software package[21,22] and B3LYP[23] and/or BPW91[24] functionals with a double zeta plus polarization (DZVP) basis set[25] for N, O, and Cl atoms, and the LANL2DZ basis set and effective core potential for the iridium atom[26]. Calculated structures and other data calculated were obtained by full optimization or by single-point calculation of the X-ray structures (Na⁺ salt and PPh₄⁺ salt with the anisotropic refinement). In all cases the stability of the wavefunction obtained from DFT calculations was tested and verified and all the integrations were performed using the Gaussian 98 tight criteria. Atomic charges have been calculated by using Mulliken and NPA[27] schemes. The background charge distribution including static contributions was performed as described under Results and Discussion[46,44]. Open-shell singlet calculations were performed under the broken symmetry formalism. A normal modes analysis was performed in order to obtain vibrational frequencies, force constants, and zero-point energy corrections for the total energy.

**Solid-state calculations were performed using the Quantum ESPRESSO package[28,29],** featuring periodic boundary conditions, plane-wave basis sets, and pseudopotentials to describe the ion-electron interactions. In the present simulations, Vanderbilt ultrasoft pseudopotentials were used[30] in combination with plane-wave kinetic energy cutoffs of 20 and 160 Ry to expand the Kohn-Sham orbitals and the charge density, respectively. For the iridium atom, a pseudopotential including nonlinear core width corrections was used.
corrections was adopted, with s and d valence electrons. All calculations were spin-polarized, based on the PBE (Perdew, Burke, and Ernzerhof) exchange-correlation functional(19) and gamma-point sampling. The experimental tetragonal unit cell was used, with lattice parameters $a = b = 12.827$ and $c = 7.087$ Å.

Acknowledgements

We are grateful to Carlos Brondino (UNL) for EPR measurements and Eckhard Bill for SQUID measurements. We thank UBA, Fundación Anhemibio and LNLS Synchrotron (Proposal XAFS 4642/05), Campinas, SP, Brazil for financial support.

[2] KBr pellet: 2006 cm$^{-1}$; CH,CN solution: 1953 cm$^{-1}$.
[3] $E_{1g} = + 0.96$ V versus Ag/AgCl in 1 M HClO$_4$; $E_{2g} = -0.33$ V versus ferrocene in butyronitrile.
[7] J. H. Enemark, R. D. Feltham, Coord. Chem. Rev. 1974, 13, 339–406. In the Enemark-Feltham notation a mononitrosyl complex is described as [MNO$^+_x$], were $n$ is the total number of electrons in the metal d and NO $\pi^*$ orbitals.
[12] $\beta$PPh$_4$; tetraphenylphosphonium; AsPh$_3$; tetraphenylarsenion.