Contribution from the Department of Chemistry, University of Leicester, Leicester LE1 7RH, United Kingdom

On the Formalism of Treating the Linear Nitric Oxide Ligand as NO^+

J. B. Raynor

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Evidence is presented to show that consideration of the linear nitric oxide ligand in transition metal complexes formally as anything other than NO^+ (e.g. NO^- or NO.) has little meaning or value. Since most inorganic chemists are more interested in electron configuration than effective charge, much confusion can be eliminated if formal oxidation numbers are consistently used and the nitric oxide ligand formally treated as NO^+.

There has been much confusion among chemists, and many papers in the literature concerning whether nitric oxide in complexes bonds as NO^+, NO. or NO^+. The dilemma originated at about the time when Lewis, Irving, and Wilkinson[1] classified the then known nitric oxide complexes into two categories according to their N–O stretching frequencies. This proved useful in that it highlighted several so-called nitric oxide complexes with unusually low ν(NO) in which it was proposed that the NO was formally bonded as NO^-. All the complexes mentioned by these authors with low ν(NO) (*i.e.* in the region 1040-1195 cm^{-1}) have since been reformulated without the need to invoke the NO^- group,[2] although a recent crystal structure redetermination has shown that $[Co(NO)(NH_3)_5]^{2+}$ has a bent Co–N–O atomic arrangement.[3] On the other hand, Gans[4] has suggested that ν(NO) frequencies in the region 1500-1700 cm^{-1} be also associated with the group bonded as NO^-. With the recent preparation and study of a number of compounds with ν(NO) around 1500-1600 cm^{-1}, fresh discussion has arisen concerning the nature of the bonding of the nitric oxide group. This paper attempts to clarify the confusion and show that reference to the nitric oxide group as NO^- or NO. is usually either wrong or meaningless. The discussion concerns only those complexes where the metal N–O atomic arrangement is linear. The existence of a number of complexes with a M–N–O bond angle around 120° is an entirely separate case and is not considered here.

It would seem that most workers who advocate the treatment of nitric oxide in complexes as NO^- mean one of two things. Either the ligand is treated formally as NO^- (containing the definite chromophore NO^- with two unpaired electrons in the doubly degenerate π^* orbital) in the same way as oxide is treated formally as O^{2-} (with a closed shell configuration), *or*, that there is a charge redistribution *via* π-back bonding from the metal $e(\pi)$ orbitals (in C_{4v} symmetry) to $e(\pi^*)$ orbitals on the ligand such that there is a net unit negative charge on the ligand but unaccompanied by any change of total spin. However, in most cases, it is not clear which meaning the author is advocating. Let us consider each in turn, taking several representative examples of each.

Jørgensen and others[4,5,6] have suggested that it migth be better to formulate the diamagnetic ion $[Pt(NO)Cl_5]^{2-}$ as Pt^{IV} and NO^- rather than Pt^{II} and NO^+. If the second formulation (d^8-NO^+) is preferred, then the electron confugration is almost certainly $e(d_{xz,yz})^4 < b_2(d_{xy})^2 < a_1(d_{z^2})^2 < e'\ (\pi^*\ NO)$ (I) and that the eight electrons are in orbitals of predominantly metal character. However, if the first formulation is preferred (d^6–NO^-), with the implication that there are two unpaired eletrons in the degenerate $e'(\pi^*NO)$ level, then this e' level must become lower than a_1 such that the configuration is $e^4 < b_2^2 < e'(\pi^*NO)^2$ (II), thus making the molecule paramagnetic (which it is not). Some authors have suggested an antiferromagnetic interaction between unpaired *d*-electrons and those on the NO^-. This is only feasible if the orbitals have the same symmetry. Such an antiferromagnetic interaction is not possible in these cases because there are no unpaired electrons on metal *e* orbitals unless the order of energy levels is drastically changed such that the b_2 and a_1 levels become lower than *e* (*i.e.* $b_2^2 < a_1^2 < e^2 < e'(\pi^*NO)^2$ (III), which seems highly improbable. Configuration (II) can be modified by further lowering of the $e(\pi^*NO)$ level so that the configuration is now $e^4 < e'^4$ (IV), but then it is only logical to refer formally to the molecule as d^4–NO^{3-}. This is clearly absurd. E.s.r. results[7] for the ion $[Cr(N)_5NO]^{3-}$, the magnetic susceptibility of which indicates one unpaired electron, show unambiguously that the best nominal formulation is Cr^I–NO^+ with the electron configu-

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(1) J. Lewis, R.J. Irving and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 7, 32, (1958); W.P. Griffith, J. Lewis and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 7, 38 (1958).

(2) J.B. Raynor, *J. Chem. Soc.* (A), 997, (1966).

(3) C.S. Pratt, B.A. Coyle and J.A. Ibers, *J. Chem. Soc.* (*A*), 2146, (1971).

(4) P. Gans, *Chem. Commun.*, 144 (1965).

(5) C.K. Jorgensen, *Inorganic Complexes*, Academic Press, London (1963); *Oxidation Numbers and Oxidation States*, Springer-Verlag, Berlin (1969).

(6) P. Gans, *J. Chem. Soc.* (*A*), 943 (1967), E.E. Mercer, W.A. Mc Allister and J.R. Durig, *Inorg. Chem.*, 6, 1816 (1967).

(7) B.A. Goodman, J.B. Raynor and M.C.R. Symons, *J.Chem. Soc.* (*A*)., 994 (1966).

ration $e(d_{xz,yz})^4 < b_2(d_{xy})^1$(V). If the formulation were Cr^{III}–NO$^-$, as suggested by Gans,[4], then there must be a lowering of the e(πNO) level such that the electron configuration is $e^3 < e'^2$ or $(b \sim e)^3 < e'^2$, assuming no antiferromagnetic interaction. If an antiferromagnetic interaction were invoked to pair the electrons, then a configuration $e^4 < e'^1$ (VIII) results. None of these configurations is compatible with the e.s.r. results.

The same type of arguments can be used to show that complexes like [Fe(NO)(NH$_3$)$_5$]Cl$_2$ are best considered[8] as Fe^I–NO$^+$ and not Fe^{III}–NO$^-$. Further examples of molecules where authors have suggested that the nitric oxide is bonded as NO$^-$ (or even NO.) are Fe(NO)(salen),[9] [Fe(NO)(H$_2$O)$_5$]$^{2+}$.[5] In no case can a suitable molecular orbital energy level scheme be proposed which is compatible with known magnetic properties. We are forced to conclude that the linear nitric oxide ligand cannot exist formally as NO$^-$, or NO. whether antiferromagnetic interactions are involved or not.

On the other hand, Brown[10] suggests that such complexes as [Fe(CN)$_5$NO]$^{2-}$ formally contain iron with an effective charge of +3 and that the linear nitric oxide ligand is a formally neutral species. The evidence for this is the chemical similarity of nitroprusside and ferricyanide and the similarity of the cyanide stretching frequencies with those of Fe^{III} cyanide complexes. (Infrared is a particularly insensitive probe for C–N stretching frequencies and in any case so many factors contribute to the strength of a bond that analysis of a stretching frequency is notoriously difficult). Mössbauer measurements are of little value in the absolute determination of electron configurations. That the isomer shift and quadrupole coupling are nearer that of typical ferric complexes than of ferrous complexes illustrates only that the nitric oxide ligand is ambivalent. Such an electronegative ligand is inevitably going do alter the charge distribution in the complex and increase the s-electron density at the nucleus. Most of these arguments, together with the evidence of the molecular orbital calculations of Manoharan and Gray[11] show that the effective charge on the metal is increased and that on the nitric oxide ligand reduced. This is not disputed, but it is a different matter to refer to it as a formal transfer of an electron from one orbital to another.

If, then, all that those workers who make reference to NO$^-$ and NO. are trying to do is to represent a transfer of charge, then it is illogical to restrict this to the nitric oxide group only. This is particularly so when there is a large transfer of charge also in, *e.g.* oxy complexes. No one would ever consider the metal in [MnO$_4$]$^-$ as Mn^I, yet from molecular orbital calculations by Viste and Gray,[12] the metal has a residual charge of +0.60 and configuration $3d^{5.81}$ $4s^{0.22}$ $4p^{0.37}$ and the oxygen atoms a charge of –0.40 each. Likewise, Nieuwpoorte[13] in calculations on [Fe(CO)$_4$]$^{2-}$ found that the metal charge is about +0.4, showing the considerable transfer of charge to the carbonyl groups. Few chemists would consider treating the carbonyl group as CO$^-$, so why should the nitric oxide group be singled out and treated other than NO$^+$ when its coordination behaviour is so similar to the isoelectronic CO and CN$^-$?

Most inorganic chemists are more interested in electron configuration than effective charge. This latter concept can be of value in accounting for and predicting trends in the chemistry of particular families of compounds but should not be confused with formal oxidation numbers and oxidation states. With this in mind the confusion over the nomenclature for the nitric oxide group can be eliminated if formal oxidation numbers are consistently used for each metal and ligand group according to the custom already in use for O^{2-}, CO, CN$^-$, etc. It follows then that for electron book-keeping purposes, the linear nitric oxide ligand is best formulated as NO$^+$, irrespective of the chemical source of the nitric oxide, and always called nitrosyl without any implication as to what the residual charge on the ligand is, but acknowledging that considerable transfer of charge is possible and, indeed, usually takes place.

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