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On the Effective Charge of Iron in Nitroprusside

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Examination of the known physical and chemical properties for the nitroprusside ion, $Fe(CN)_5NO^{2-}$, demonstrates that this species formally contains iron with an effective charge of +3. In particular, comparison to the series $Fe(CN)_5X^{n-}$ leads to the conclusion that nitroprusside must be grouped with the ions known to contain Fe^{3+}, and that its formulation as a Fe^{2+}–NO^+ complex is misleading.

Introduction

Although the idea of the charge on a metal in a complex is a formalism, it is nonetheless a useful concept. Many properties of metal complexes can be correlated on the basis of an integral effective charge, and metal ions in complexes are routinely described in these terms. Although in most cases the assignment of a charge to the metal is straightforward, in ambiguous cases the best approach is through analogy to compounds where no such ambiguity exists, and that is the approach of this paper.

For the extremely important class of metal complexes containing the nitrosyl group as a ligand, normal methods for assigning an effective charge to the metal are inadequate, since nitric oxide can be considered to bond formally as either NO^+, $NO\cdot$, or NO^-. One of the most common nitrosyl complexes is the nitroprusside ion, $Fe(CN)_5NO^{2-}$, and this species is often used as a model for the bonding of nitric oxide to metals. For the three charge types of nitrosyl mentioned above, the effective charge of iron in nitroprusside becomes +2, +3, or +4. Unfortunately, there seems to be no real concensus on which is the correct description, and nitroprusside is routinely described in the literature both as a +2 and a +3 species.

Two other observations are commonly used to decide upon the effective charge of iron in this species. The N–O stretching frequency in nitroprusside is 1940 cm^{-1}, which is one of the highest frequencies observed for coordinated nitrosyl.[1] Since the unpaired electron in nitric oxide lies in a π^* orbital, its removal to form NO^+ leads to an increased bond order, hence frequency. Thus, several correlations of N–O stretching frequency *vs.* charge type have been proposed,[2] all of which agree that the observed frequency in nitroprusside indicates NO^+ and, as a consequence, Fe^{2+}. The other observation is the diamagnetism of nitroprusside, which is consistent with Fe^{2+} or Fe^{4+} in C_{4v} symmestry, but is generally considered to rule out Fe^{3+}, which is a d^5 system and expected to be paramagnetic. Coupled with the infrared data, this line of reasoning leads to the formulation of nitroprusside as a Fe^{2+}–NO^+ species. It is the purpose of this communication to present some of the chemical and physical data which demonstrates that the effective charge of iron in nitroprusside is actually +3.

As early as 1900, Hofmann[3] found that the reactions of metal ions and nitroprusside or its analogs, $Fe(CN)_5X^{n-}$, $X = H_2O$, NH_3, NO_2^-, *etc.*, gave products which were characteristic of the effective charge on the iron. The reactions of nitroprusside with transition metals form solid products similar to Prussian blue and its analogs,[4] as indicated by their ready precipitation, colors, face-centered-cubic lattices, and increase in ν_{CN} of about 30 cm^{-1} (characteristic of bridging cyanide) upon complex formation.[5,6,7]

Hofmann[3] showed that in all such reactions, the nitroprusside ion was acting like ferricyanide, rather than like ferrocyanide. For example, the reaction of ferric chloride with all the Fe^{2+} analogs, $Fe^{2+}(CN)_5X^{n-}$, gave deep-blue precipitates similar to Prussian blue, whereas with ferricyanide and nitroprusside it gave only brown solutions. Similar reactions with other metals leave no doubt that in these complexes at least, nitroprusside behaves as a Fe^{3+} species.

Infrared spectra of nitroprusside and its analogs lead to the same conclusion. For hexacyanometallates the cyanide stretching frequency is characteristic of the effective charge on the metal to which the cyanide is bound.[8] Thus, $K_4Fe(CN)_6$ absorbs at 2044 cm^{-1}, $K_3Fe(CN)_6$ at 2118 cm^{-1},[9] and $K_2Pt(CN)_6$ at 2190 cm^{-1}.[9] The same charge dependency holds for the nitroprusside analogs $Fe(CN)_5X^{n-}$, as is evident from Table I. The observed frequency for nitroprusside[10] indicates clearly that it should be grouped with the species known to contain Fe^{3+}. Consistent with this, it has previously been observed[1,11] that the shape and intensity, as well as the position, of the cyanide stretching band in nitroprusside resemble those observed

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(1) G. Bor, *J. Inorg. Nucl. Chem.*, *17*, 174 (1961).
(2) B.F.G. Johnson and J.A. McLeverty, *Progr. in Inorg. Chem.*, F.A. Cotton ed., *7*, 277 (1966).
(3) K.A. Hofmann, *Justus Liebigs Ann. Chem.*, *312*, 1 (1900).
(4) D.B Brown and D.F. Shriver, *Inorg. Chem.*, *8*, 37 (1969).
(5) L.A. Gentil, E.J. Baran, and P.J. Aymonino, *Z. Naturforsch.*, *23b*, 1264 (1968).
(6) J.B. Ayers and W.H. Waggoner, *J. Inorg. Nucl. Chem.*, *31*, 2045 (1969).
(7) P G. Salvadeo, *Gazz. Chim. Ital.*, *89*, 2184 (1959).
(8) L.H. Jones, *Inorg. Chem.*, *2*, 777 (1963).
(9) D.B. Brown and M.B. Robin, unpublished observations.
(10) Under high resolution, four C-N stretching frequencies are observed for nitroprusside.[1] However, the use of this data in Table I in place of the low-resolution data would have no effect on any of the conclusions.
(11) E.F.G. Herington and W. Kynaston, *J. Chem. Soc.*, 3555 (1955)

Table I. Infrared data for nitroprusside analogs, $Fe(CN)_5X^{n-}_{}$.

	ν_{CN}		δ_{MCN}		ν_{MC}		Reference
X	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	
H_2O	2058	2121	571	535	410	412	1,2
NO_2^-	2071	2123	572	500	430	408	1
NH_3	2046	2116	569	521	408	409	1
SO_3^{2-}	2052		577		405		2
CN^-	2050	2115	590	520	419	390	1,2
NO		2141		525		425	1

(1) W Haberditzl, W. D. Schleinitz, and H. G. Bartel, *Z. Naturforsch.*, *23b*, 891 (1968). (2) L. Tosi and J. Danon, *Inorg. Chem.*, *3*, 150 (1964).

Table II. Mössbauer parameters for nitroprusside analogs, $Fe(CN)_5X^{n-}$.

	δ(mm/sec)		ΔE(mm/sec)	
X	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
H_2O	0.27	0.12	0.80	1.82
NO_2^-	0.22	0.12	0.89	1.78
NH_3	0.31	0.12	0.70	1.78
SO_3^{2-}	0.22		0.80	
NO		0.00		1.85

for the known Fe^{3+} analogs. The one-electron reduction product of sodium nitroprusside has recently been isolated as the tetraethylammonium salt,[12] and in agreement with the trends of Table I, exhibits a cyanide stretch at 2075 cm^{-1}, consistent with the presence of Fe^{2+}. Although the cyanide stretching region is most characteristic of the effective charge on the metal, further correlation can be obtained at lower frequencies. The absorption which is primarily a MCN bending mode[13] separates the two charge types, falling between 569-590 cm^{-1} for the Fe^{2+} complexes, and between 500-535 cm^{-1} for Fe^{3+}. Again, the value of 525 cm^{-1} observed for nitroprusside classifies it as a Fe^{3+} complex.

The two arguments given above yield information from the properties of the complex ion as a whole and from the properties of a ligand external to the questionable portions of the complex. A third technique, Mössbauer spectroscopy, is a probe to the metal itself. Although the Mössbauer spectrum of nitroprusside has generally been interpreted on the assumption that it contains Fe^{2+}, examination of the data[14] in Table II leads to its classification as Fe^{3+}. The isomer shift data for nitroprusside does not fall within the range of either the Fe^{2+} or Fe^{3+} complexes, lying instead more toward what would be a Fe^{4+} complex. It is, however, much more consistent with Fe^{3+} than with Fe^{2+}. Quadrupole splittings divide into two well-resolved groups which appear to depend only on the iron effective charge, and not at all on the nature or charge of the ligand X, and the quadrupole splitting for nitroprusside falls with those of the +3 complexes.

There is more Mössbauer data which can be interpreted to indicate that nitroprusside contains Fe^{3+}. Drickamer and co-workers[15,16,17] have investigated the effect of high pressures on the Mössbauer spectra of ferro- and ferricyanides and their substitution products, and find a number of general reactions. For metal ferrocyanides, the application of high pressures and elevated temperatures leads to partial conversion to high-spin Fe^{2+}. For ferricyanides, there is reduction at room temperature and high pressure to low-spin Fe^{2+}, and at higher temperatures this reduced form then acts in the same fashion as the ferrocyanides, giving high-spin Fe^{2+}. Using these systems as models, the data for the nitroprussides can be consistently interpreted if nitroprusside is considered to be a complex of Fe^{3+}. Two things happen when the nitroprussides are subjected to high pressures and elevated temperatures. First, a new peak, ascribed to low-spin Fe^{2+}, appears with an isomer shift slightly higher than nitroprusside, and nearly identical to that of the Fe^{2+} complex $Na_3Fe(CN)_5NH_3$. Although this appears as a single peak, the authors note that a modest quadrupole splitting might be involved, but would be impossible to resolve in the complex spectrum. The existence of this peak is compatible with reduction from Fe^{3+} to Fe^{2+} just as in the ferricyanides, only here the extent of reduction can be readily determined, since the large quadrupole splitting of nitroprusside effectively separates the low-spin Fe^{2+} and Fe^{3+}. For $Na_3Fe(CN)_5NH_3$, which unquestionably contains iron with an effective charge of +2, no such phenomenon occurs, nor would it be expected to. A sample of a nitroprusside complex treated so as to produce the maximum amount of the low-spin Fe^{2+} species and then quenched to room temperature and atmospheric pressure exhibited an infrared spectrum consistent with the interpretation given here. This material contained a new strong band at 2076 cm^{-1}, which is what is expected for nitroprusside reduction, and which agrees well with the value of 2075 cm^{-1} for the chemically reduced species.[12] As expected in light of the results on the ferrocyanides and ferricyanides, the nitroprussides and $Na_3Fe(CN)_5NH_3$ both produce high-spin Fe^{2+} at higher temperature and pressures.

Although the evidence given above is the most compelling, one other piece of information should be mentioned. Nitroprusside acts as if it has the same size as ferricyanide. It has previously been shown[4] that in complexes with structures analogous to that of Prussian blue, ferricyanide has an effective radius of

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(12) R. Nast and J. Schmidt, *Angew. Chem. Internat. Edit.*, *8*, 383 (1969).

(13) The assignment of this mode to MCN bending is not definite, and in fact Ref. 8 assigns it to MC stretching. The assignment is not critical to the conclusions of this paper.

(14) N.L. Costa, J. Danon, and R.M. Xavier, *J. Phys. Chem. Solids*, *23*, 1783 (1962).

(15) A.R. Champion and H.G. Drickamer, *J. Chem. Phys.*, *47*, 2591 (1967).

(16) S.C. Fung and H.G. Drickamer, *ibid.*, *51*, 4353 (1969).

(17) S.C. Fung and H G. Drickamer, *ibid.*, *51*, 4360 (1969).

4.45 Å, whereas ferrocyanide has an effective radius of 4.33 Å. Using the published data[5] for the metal nitroprussides with this structure, an effective radius for nitroprusside of 4.48 Å is obtained, making it approximately the same size as ferricyanide.

The data discussed above lead to the conclusion that nitroprusside contains iron with an effective charge of +3, but it is still necessary to rationalize the observed N–O stretching frequency and diamagnetism of the complex. Free NO absorbs at 1876 cm^{-1}, whereas NO$^+$ absorbs at 2220 cm^{-1}.[18] Formal transfer of the π^* NO electron to Fe^{3+} to produce Fe^{2+} and NO$^+$ should lead to a large increase in frequency, and the small observed increase (to 1940 cm^{-1}) indicates a bond order much closer to that in NO than to that in NO$^+$. Nor is the diamagnetism of this species inconsistent with an effective charge of +3 on iron, since with an even *total* number of electrons the complex may be either diamagnetic or paramagnetic, depending upon the particular arrangement of the molecular orbitals. The molecular orbital calculations of Monoharan and Gray,[19] which are often invoked as proof for Fe^{2+} in nitroprusside, show a perfectly reasonable ordering. Of interest to the arguments here, however, is the electron population in the π^* NO level, which is very close to unity. The next to highest occupied orbital (designated 6e) is composed primarily of metal d_{zx} or d_{yz}, but is 24.8% π^* NO. The four electrons in this orbital thus give a formally neutral NO, and Fe^{3+}. Phrased in qualitative terms, the unpaired electron on Fe^{3+} in the strong-field C_{4v} environment forms an electron pair bond with the unpaired electron in the π^*-orbital on NO, yielding no electron transfer, but leading to a diamagnetic system. This description (the molecular orbital description leads to an equivalent conclusion) predicts what is nominally a double bond between Fe and N. The observed distance of 1.63 Å[20] is significantly shorter than the Fe–CN bond length of 1.90 Å, which would be expected to be a lower limit for the bond length between Fe and the isoelectronic NO$^+$. Thus, considerable double bond character is indicated.

A recent review[21] has presented evidence, primarily on electrochemical grounds, that the formal oxidation state of iron in intropresside is +2. It is, however, possible to interpret the two major arguments of the review as consistent with an effective charge of +3 on iron. For the free nitrosyl group the equilibria (1) exist,

$$NO^+ \underset{OH^-}{\overset{K_1}{\rightleftharpoons}} HNO_2 \underset{OH^-}{\overset{K_2}{\rightleftharpoons}} NO_2^- \qquad (1)$$

and analogous equilibria (2) exist

$$[Fe(CN)_5NO]^{2-} \underset{OH^-}{\overset{K'_1}{\rightleftharpoons}} [Fe(CN)_5NO_2H]^{3-} \underset{K'_2}{\overset{OH^-}{\rightleftharpoons}} [Fe(CN)_5NO_2]^{4-} \qquad (2)$$

for nitroprusside, leading Mašek to conclude that NO in nitroprusside is behaving as NO$^+$. However, if this is the case then at least the ratios K_2/K_1 and K_2'/K_1' should be nearly the same. The observed values ($pK_1 = -7.86$, $pK_2 = 3.4$, $pK_1' = 17.4$, $pK'_2 = 6.4$) demonstrate that although there is relatively little difference between K_2 and K_2', a factor of 10^{25} separates K_1 and K_1'. This is reasonable if it is assumed that the first step of equilibria (2) requires, in addition to the analogous step in equilibria (1), significant electronic reorganization of the system to produce a species with an effective charge of +2 on iron and, consequently, NO$^+$. The second argument is based on reduction potentials, and here again the data appears consistent with an effective charge of +3 for iron in nitroprusside. Although the second reduction potential for NO$^+$ and nitroprusside are nearly identical, the first reduction potentials are significantly different (+1.18 V. and –0.365 V., respectively) indicating that the reactions are not equivalent. This is reasonable if the initial reduction of nitroprusside is considered in a formal sense to be a reduction of the metal to Fe^{2+} and not of NO$^+$ to NO.

The evidence presented here, which points to an effective charge of +3 for iron in the nitroprusside ion, indicates that in this compound at least nitric oxide bonds as a formally neutral species. No inference can be made about the mode of bonding of NO in any of its other complexes, but the data do point out the difficulties inherent in assigning electron configurations and charges on metals from the measurement of one parameter external to the metal.

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[18] K. Nakamoto, «Infrared Epectra of Inorganic and Coordination Compounds», John Wiley and Sons, New York (1963), p. 72.

[19] P.T. Monoharan and H.B. Gray, *J. Am. Chem. Soc.*, *87*, 3340 (1965).

[20] P.T. Monoharan and W.C. Hamilton, *Inorg. Chem.*, *2*, 1043 (1963).

[21] J. Mašek, *Inorg. Chim. Acta Reviews*, *3*, 101 (1969).