

COMMENT

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rsc.li/daltonReply to the 'Comment on "In Defence of
Oxidation States"' by J. C. Green, *Dalton
Transactions*, 2022, 51, DOI: 10.1039/D1DT02930DNicholas C. Norman* and Paul G. Pringle  *

We reiterate and reinforce some of the points concerning oxidation states and the Covalent Bond Classification method we made in the Perspective article entitled 'In Defence of Oxidation States' including a brief discussion of the relative merits of the terms 'metathesis' and 'redox' when considering addition across a metal–metal bond.

In our recent Dalton Perspective entitled "In Defence of Oxidation States" (N. C. Norman and P. G. Pringle, *Dalton Trans.*, 2022, 51, 10.1039/D0DT03914D),¹ we did indeed mount a defence of oxidation states, not in response to any widespread assault on the concept but rather, as we said in the article, because their value had been questioned by some of the advocates of the Covalent Bond Classification (CBC) method, not least on pedagogical grounds. At the time of submission, we specifically requested that someone who may have a different view from us be offered the opportunity to respond formally by way of a Dalton Comment and we therefore welcome the response from J. C. Green and offer this Reply by way of return.

There is little within Green's Comment² with which we would disagree. The opening paragraph which outlines the origins of the CBC method during the 1970s is both interesting and informative and we do appreciate and recognize the contribution the CBC method has made especially in categorising organotransition metal compounds; we say so, in the introduction and in the concluding remarks.¹ We recognize also the value of the so-called MLX plots, which plot Valence Number (VN) against Electron Count, and concur with the reasons Green offers to demonstrate the insight they afford. We would argue, however, that a related plot which employs Oxidation State (OS) rather than VN would provide similar insights, in large part because, as Green states (and we agree), VN and OS values are the same in many compounds. Differences between plots based on either VN or OS would be expected for metal–metal bonded compounds for the reasons we¹ and Green² discuss, but a more significant divergence would be apparent for compounds in which the element in question is in a negative oxidation state. In this latter

case, the principal difference would be that, in a plot based on OS, there would be rows for negative values which do not and cannot occur in a plot based on VN since, by definition, VN cannot be negative. Moreover, as we stated in our Perspective,¹ any application of the rules used to assign an Equivalent Neutral Class (ENC) and derived VN for compounds which exhibit negative oxidation states leads to an erroneous d^n number, although we offered a simple resolution to this problem (see ref. 21 and 22 in ref. 1).

We and Green agree that compounds such as Hg_2Cl_2 and $\text{Mn}_2(\text{CO})_{10}$ which contain metal–metal bonds are treated differently by the OS and CBC methods.³ Regarding the assignment of the d^n number in the Mn example, we also agree that the CBC method affords a more direct approach to its determination, but we maintain that the use of oxidation states offers a better insight into the chemistry of such species. One can indeed, as Green suggests, classify the reaction between Hg_2Cl_2 and Cl_2 to give HgCl_2 as a metathesis reaction in which the VN of the Hg remains unchanged but it is our contention that a description in terms of oxidation states benefits from placing such a reaction within the universal framework of oxidation and reduction (redox) reactions.

Green's penultimate paragraph relates to ligands that are problematic for both the OS and the CBC methods, perhaps chief amongst these being the nitrosyl ligand, NO. In our Perspective,¹ we address NO in some detail and, while it may be the case that NO should be considered as an X_3 ligand in $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})]$ as Green has reported,⁴ or sometimes as an LX ligand in other compounds,² we would argue that in those we highlight,¹ it should be regarded as an L^+ ligand but where L^+ is not equivalent to X for the purposes of calculating an ENC and a derived d^n number.

In Green's concluding paragraph, the point is made that when issues arise which pose a problem for simple models, it is an invitation to examine the compound(s) using more soph-

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isticated models. We agree entirely and have highlighted examples where both the OS and CBC models struggle. As we said in our article, however, we should not judge either of the models too harshly in such circumstances. There will always be exceptions which expose the limitations of simple models and the challenge we all face as educators is to instill a confidence in our students which allows them to use a particular model in appropriate circumstances whilst being fully aware of its limitations.

Conflicts of interest

There are no conflicts of interest to declare.

References

- 1 N. C. Norman and P. G. Pringle, In Defence of Oxidation States, *Dalton Trans.*, 2022, 51, DOI: 10.1039/D0DT03914D.
- 2 J. C. Green, Comment on 'In Defence of Oxidation States' by N. C. Norman and P. G. Pringle., *Dalton Trans.*, 2022, 51, 10.1039/D0DT03914D, *Dalton Trans.*, 2022, 51, DOI: 10.1039/D1DT02930D.
- 3 In ref. 23 in ref. 1 above, we state, 'To the best of our knowledge, this adjustment of the d^n configuration specifically in binuclear, metal-metal bonded complexes has not previously been suggested' when discussing the d^6 configuration of the Mn centres in $Mn_2(CO)_{10}$. There is, in fact, a brief discussion of this topic in *Orbital Interactions in Chemistry*, T. A. Albright, J. K. Burdett and M. H. Whangbo, Wiley Interscience, 1985. Please also note that in ref. 1, Ti(IV) in the caption for Figure 3 should read Zr(IV).
- 4 C. N. Field, J. C. Green, M. Mayer, V. A. Nasluzov, N. Rösch and M. R. F. Siggel, Study of the Electronic Structure of Ni (η^5 -C₅H₅)(NO) by Variable Photon Energy Photoelectron Spectroscopy and Density Functional Calculations, *Inorg. Chem.*, 1996, 35, 2504–2514.

