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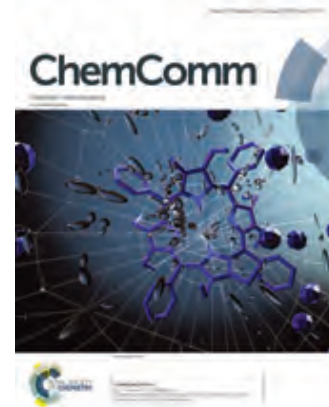
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triphenylene trisemiquinone bridged Ni3 complex

We thank the reviewers for their work and constructive comments that helped
to improve the manuscript. We agree with most of the comments of reviewer
1, however there are some points raised with which we do not agree.
We answer, below, all the points raised by the reviewers and we correct the
manuscript accordingly.

Referee: 1

Comments to the Author
This manuscript by T. Mallah and coworkers reports on electronic and
magnetic properties of a trinuclear nickel(II) complex with
hexahydroxytriphenylene. This type of systems is gaining renovated interest
in these times due to their possible application as models for spin
interactions in 2D electrically conductive MOF (as in the very recent ref.
8) or as possible building blocks of quantum gates which can be perturbed
and controlled by electric field. As such, it would be justified to publish
it in Chemical Communications. However, in its present version the analysis
of the magnetic properties of the system is not very sound, and neglects
quite a large part of the literature of the past quarter of century on
Ni(II)-semiquinonato systems. The manuscripts thus require major revision
before acceptance.
As a first point, I note that authors simply state that the differences in
Ni-O and C-C distances are consistent with sq character of the bridging
ligand, while it is the absolute value of C-C and C-O distance which
unequivocally indicate this, as well known in literature on metal-sq
systems (see e.g. Brown, S. N. Inorg. Chem. 2012, 51, 1251-1260, and C. G.
Pierpont, Coord. Chem. Rev. 2001, 216-217, 99).

Answers:
This is not exactly what was stated in the original version. We did not
write that it is the difference between the Ni-O and C-C bond distances
that are consistent with the semi-quinone character. The semi-quinone
character is clear from the values of the C-O and C-C bond distances, this
is clear but we will insist more on this point by adding a sentence in the
revised version and we will add the relevant references in the literature
that support this. Our point goes beyond the (obvious) fact that we have
semiquinone character for the three groups. We pointed out (and this is
clear in the original version) that the DIFFERENCE between the two C-O bond
distances around one of the Ni ions (Ni1) is larger than this same
difference around Ni2 and Ni3 and also the DIFFERNCE between the two Ni-O
bond distances around Ni1 is larger than these differences around Ni2 and
Ni3 leading to the conclusion that the semiquinone character is more
pronounced around Ni1 (that has a geometry closer to tbp) than around Ni2
and Ni3 (that have a geometry very close to spy). So, the point was to see
if, from structural data, it was possible to see if the semiquinone
character is more (or less) pronounced around some of the
crystallographically different Ni atoms. And, indeed, this semiquinone
character is more pronounced around Ni1 leading to the conclusion that the
electronic density is more localized around Ni1 (tbp) than around Ni2 and
Ni3 (spy). This idea is very important because we have here an example of a
conjugated ligand with a trisemiquinone character in trinuclear Ni(II)
complex and we have its crystal structure (for the first time), which
allows to get insight from the structure on the electron delocalization of
the electrons of the three semiquinone species with the respect to the
Ni(II) ions. I see that we summarized too much the idea in the original

version, so we will add some sentences for the idea to be clear and we will add the relevant references.

From structural data analysis, the ligand is in the tris-sq state, which might lead an uniformed readder to think that a triradical sttate is attained. This is clearly not the case, but a short explanation on this point is on my opinion essential. Indeed, this is of the utmost importance to understand the reason of the use of the specific spin hamiltonian in the analysis of the magnetic data of 1.

Answer:
We completely agree with the reviewer that one may assume that we have a triradical, which cannot be the case and, indeed, the idea that two of the electrons pair up must be introduced before the magnetism part. A sentence is added in the revised version just after the structural analysis part

Concerning this point, the number of parameters used for the fit of the magnetic data is far too high (3 different coupling constants + 3 different g values for Ni(II) centers + 3 different D values + TIP) and can be highly correlated: it is not even clear whether they were all left free or not (no error bars are given for the best fit values). This is of particlar relevance since the fit of the magnetic data provide results which are not in line with expectation from simple magnetostructural correlations for Ni(II)-sq exchange. In particular, it is well known that for square pyramidal (or distorted octahedral) Ni(II) systems, the interaction with SQ radical is expected to be ferrromagnetic (see eg Inorg. Chem. 2002, 41, 1086-1092 for an example of Ni(II)3SQ3 complex), while for tbp is antiferromagnetic (see eg Dei, Gatteschi Inorg. Chim. Acta 198-200 (1992) 813-822).
The corresponding hamiltonian should then feature an isosceles triangular symmetry with J1=J2 ferromagnetic, and J3 antiferromagnetic. Any deviation from such expectation should be critically analyzed and discussed using simple symmetry based arguments. If this is not possible now, then authors should wait to have their theoretical calculations finished and include them (there is plenty of space before reaching the 4 pages limit of ChemComm). This might also explain the huge TIP value used to fit the data, which accounts for 25% of the magnetic susceptibility at room temperature, and at the moment has no physically sound explanation.

Answer:
We agree with the reviewer that we had many parameters and that these parameters can be correlated. That is why when performing the fitting procedure, we had to restrict some parameters within a given range justified by their structure and by results from the literature. We made restriction for the g parameters between 2.0 and 2.4, which is reasonable for Ni(II) in pentacoordinate environment. We restricted the D values between 10 and 30 for Ni2 and Ni3 (spy) and between -10 and -40 for Ni1 (tbp). *We already mentioned this restriction on D values in the original version*. Again these ranges are those expected for the two different geometries based on recent reports by us and others on ZFS of pentacoordinate Ni(II) complexes. Finally, TIP and J values were left free. We carried out extensive fitting exploring the space of phases starting from different J values. We found that there are ranges of the different J values that give reasonable fits of the experimental data BUT with J1 (with the pseudo tbp Ni1) antiferromagnetic and relatively large and J2 and J3 that are much weaker and can be ferro-or antiferromagnetic. This is done in the revised version.
The reviewer states that the coupling between the sq and a spyNi complex must be strongly ferromagnetic as for octahedral Ni complexes. While, the coupling between tbpNi and sq must be antiferromagnetic. Our results are in line with the last statement where we indeed find large antiferromagnetic

coupling between the pseudotbpNi and sq. For the coupling between
pseudospyNi and sq, we do not find a lager ferromagnetic coupling as the
reviewer thinks it should be, the coupling is rather weak and may be ferro-
or antiferro.
We looked back in the literature and considered the reference suggested by
the reviewer. Actually, not much is known concerning the relation between
geometry and exchange coupling in *pentacoordinate* Ni-sq complexes. There
exist three such complexes reported and only two structures. The oldest
compound that the reviewer mentioned (Ni(n3)(DTBSQ)(ClO$_4$) by C. Benelli et
al. Inorg. Chem. (1990), 29, 3409 and Dei, Gatteschi Inorg. Chim. Acta
(1992) 813-822) where Ni is assumed to be pentacoordinate (and which is
probably the case) has *no reported structure* so one cannot unambiguously
know whether the geometry is tbp or spy or intermediate. Our experience in
pentacoordinate Ni(II) complexes tells us that tbp Ni(II) complexes are
extremely difficult to obtain (see B. Cahier et al. Chem. Eur. J. 2017, 23,
3648 – 3657). Only when bulky ligands where steric hindrance overcome the
better electronic stabilization of spy geometry is present, tbp or pseudo-
tbp complexes are obtained. Actually, there is a contradiction between the
conclusion on the geometry of this compound (Ni(n3)(DTBSQ)(ClO$_4$)) between
the two papers mentioned above; the first paper (C. Benelli et al. Inorg.
Chem. (1990), 29, 3409) concludes that the geometry is spy based on EPR,
while the second of the same authors (Dei, Gatteschi Inorg. Chim. Acta
(1992) 813-822) concludes that the geometry is tbp, also based on EPR.
Saying all that, there is an experimental definitive result concerning this
compound is that the exchange is strongly *anti*ferromagnetic when Ni(II) is
in a pentacoordinate geometry, while it is accepted that for octahedral Ni-
sq complexes, the coupling is rather ferromagnetic and large (relevant
references are added in the revised version.
We, therefore, explored the literature and the CCDC base looking for
*penta*Ni-semiquinone complexes with structure reported. We found only two
complexes one with a quasi-spy geometry (Addison parameter tau=0.05) that
presents, on the basis of solution NMR study (220-290 K) and then confirmed
by DFT calculation (C. Cox et al., Polyhedron *162*, (2019), 165-170), a
strong *antiferromagnetic* exchange coupling. Therefore, the coupling between
a spyNi and semiquinone is antiferromagnetic and ferromagnetic as in
octahedral Ni complexes. The other complex we found has a geometry closer
to tbp (Addison parameter 0.63 very close to that of Ni1 0.65) and where
the coupling is also strongly antiferromagnetic. So in conclusion, it
appears that for pentacoordinate Ni-sq complexes, the exchange coupling
parameter is antiferromagnetic whether the geometry is pseudo square
pyramidal or trigonal bipyramidal and can be very strong.

Our results are not in contradiction with those of the literature and the
antiferromagnetic coupling between a distorted spyNi and semiquinone was
justified by DFT calculations (C. Cox et al., Polyhedron *162*, (2019), 165-
170). However, the comparison between our complex and those of the
literature is not straightforward because of the degree of delocalization
of the semiquione electron is not the same on the HHTP ring and on a
terminal DBSQ$^{·-}$ and this may change the magnitude and also the nature of the
coupling.
In conclusion to this important (and long I am sorry for that) part, our
results are in line with the literature data and the fact that the coupling
(antiferromagnetic) is not as large as in the literature is due to the
larger delocalization of the single electron of on the large HHTP^{3-} ligand.
We will correct the text in the revised version in order to express in a
clearer manner the ideas and we will site the relevant literature.
The only point that is not clear to us is the large TIP value that is
perfectly reproducible on three different samples where we took care to
have very good data in the high temperature range. We think that this may
be due to the presence of close excited states due to metal-to-ligand and
more probably to ligand-to-ligand charge transfer that may contribute to

the temperature independent paramagnetism. Actually, the recently published
paper on the Cu(II) trinuclear complex has also large TIP value. This will
be mentioned in the revised version.
Finally, calculations are crucial but are out of the scope of a Chem Comm.
The problem is that we cannot treat the three Ni-sq species alone, one
needs treating the whole molecule, which is long and tedious and probably
DFT may not be adapted because different functionals seem to lead to
different results (preliminary calculation we performed). We may need to
use WF based calculation and probably at the CASPT2 (or NEVPT2 in ORCA)
level to be able to get a reliable electronic description together with
reliable values of the exchange coupling parameters. We are working on
that.

As a final point, the reported EPR spectrum of the doubly reduced species
is analyzed by using Ni(II) antiferromagnetically coupled to a SQ: this
should then be, according to magnetostructural correlations mentioned above
and chemical/statistical arguments the tbp Ni(II) centre; but then the D
value should be negative at variance with best simulation parameters.

Answer:
No, we do not agree. The reviewer is basing his/her argument on the fact
that the coupling is antiferromagnetic only when Ni(II) has a geometry
close to tbp and not to spy. As we mentioned above, the coupling between
Ni(II) and sq can be strongly *anti*ferromagnetic also when the geometry is
spy (C. Cox et al., Polyhedron *162*, (2019), 165-170). So our result is in
line with the literature and a very strong antiferromagnetic coupling with
the spy Ni(II) is possible; the authors estimate $-1000 < J < -500$ cm^{-1}.
Finally, the average g value for Ni obtained from the EPR spectra is 2.15
which is compatible with a geometry close to spy than to tbp (a relevant
ref. will be added in the revised manuscript). So our result stating that
we have a large antiferromagnetic coupling between a pseudospyNi and
semiquinone is perfectly in line with the literature and justified by
symmetry arguments (see C. Cox et al., Polyhedron *162*, (2019), 165-170)

 I also notice that the obtained rhombicity for g value appears to be quite
high for Ni(II). In this respect, I strongly suggest that this spectrum is
simply analyzed in term of an anisotropic doublet, and then use of
projection coefficient reported in ref. 15 can be used to derive the
corresponding anisotropic g values of the single Ni(II) ion.

Answer:
We agree with the reviewer. This is actually what we have done, but have
not explicitly developed it in the paper.
So, we have first simulated the spectrum in term of an anisotropic doublet
and extracted the three g components. We will add this spectrum together
with the experimental one in the SI of the revised version. Then, we used
the projection coeff of ref. 15 (geff = -g(1/2)/3 + 4g(Ni)/3) and computed
the values of the g_{Ni} components assuming that g_{rad} isotropic and equal to 2.
We took these values and simulated the experimental spectra with different
J/D values (the spectra depend only on J/D as explained in ref.15 of the
original ms) with negative and D positive and negative. J was taken
negative (antiferromagnetic) because the positive solution leads to a
completely different spectrum.
The next step was to adjust the experimental spectrum to the simulation
with different D values and it was clear that this was possible only with
positive D values and with |J|/D around 20. The conclusion is that in the
two-reduced species, the single electron on HHTP^{3-} interacts strongly
antiferromagnetically with one of the pseudospyNi(II) while it had an
antiferromagnetic coupling coupling with the pseudotbpNi(II) in the

pristine species showing a different spin localization between the two species.

We will revise this part explaining the methodology we used as required by bthe reviewer.

Concerning the high rhombicity of the g value of a pseudospy-Ni(II) mentioned by the reviewer. Actually, even though the geometry is close to spy, it is highly distorted. The N_2O_2 plane of the spy is made of electronically different atoms (two O with one negative charge and two neutral nitrogen atoms). The angles around the Ni2 and Ni3 atoms in the plane range from 82 to 95°. In addition, the angle between the normal to the N_2O_2 plane and the apical Ni-N direction of the spy is around 10°. The structural (and electronic) parameters shows that the geometry around Ni2 and Ni3 is well distorted from the pure square pyramidal geometry and is responsible of the large rhombicity of the pseudo spy-Ni. We added some sentences in the description of the structure to highlight this distortion from the pure square pyramidal geometry.

Referee: 2

Comments to the Author
Authors reported a trinuclear Ni(II) complex bridged by trisemiquinone. Its structure and magnetic properties were characterized well. In addition, reversible electrochemical response was demonstrated by EPR spectra well. These results would give significant information for designing new switching molecules.
In my opinion, this paper is acceptable for publication in Chemical Communications after a minor revision.
Comment
Why are the J, D and g values for Ni2 and Ni3 so different? Are there notable structural difference between Ni2 and Ni3? In addition, the magnetization value at 2 K and 6 T (2.4 Bohr Magneton) is larger than the expected value based on the J values (two antiferromagnetic and one ferromagnetic). Although authors said "This solution was discarded." in SI, the simulation results would mislead readers. It needs more careful and adequate explanation.

Answer:
We agree with the reviewer that putting one of the solutions of the fitting and then discarding it adds confusion so this part will be removed in the revised version. To answer the reviewer question on why this solution was discarded: it is mainly because the D values between of Ni2 and Ni3 are different and this is not physically sound since their geometry is very close. Concerning the difference in the J values, this expresses the delocalization of the single electronic spin over Ni2 and Ni1 that can be different. Actually, since the molecule does not have a symmetry plane there is no reason that the coupling is the same.

COMMUNICATION

Electronic and spin delocalization in a switchable trinuclear triphenylene trisemiquinone bridged Ni₃ complex

Yiting Wang,[a] François Lambert,[a] Eric Rivière,[a] Régis Guillot,[a] Christian Herrero,[a] Antoine Tissot,[b] Zakaria Halime,[a] Talal Mallah[a]*

A trinuclear triphenylene trisemiquinone complex containing paramagnetic Ni^{II} is obtained under ambient condition from the reaction of the deprotonated tricatecholate hexahydroxytriphenylene (H$_6$HHTP) with Ni^{II} capped with a trispyrazolyl borate tridentate ligand. The magnetic and EPR data are consistent with a delocalization of the electronic spin over the three Ni^{II} species. The two-electron reduced complex shows an EPR spectrum corresponding to a S = ½ species due a large antiferromagnetic coupling between the radical and only one of the Ni^{II} ions highlighting the localization of the electronic spin. No EPR signal is observed for the one- and three-electron reduced species consistent with the closed shell of the bridging ligand.

Addressable molecular species, particularly electrically, are relevant to the field of quantum information because they allow, upon the application of an electrical perturbation potential, creating entangled quantum bits and, therefore, building quantum gates.[1, 2] Binuclear paramagnetic metal ions containing species have been recently reported where, upon reduction of the bridging ligand, a large exchange coupling interaction between the metal ions was observed.[3, 4]

Highly conjugated triphenylene ligands and particularly the tricatecholate 2,3,6,7,10,11-hexahydroxytriphenylene (H$_6$HHTP; C$_{18}$O$_6$H$_{12}$) are well suited for the design of trinuclear complexes with different ligand centered oxidation states. There are six accessible states that can be accessed by oxidizing HHTP^{6-} ([cat-cat-cat]; cat = catecholate) to HHTP ([q-q-q]; q = quinone). Trinuclear complexes based on H$_6$HHTP were already reported with diamagnetic metal ions (Ru^{II} and low spin Co^{III}) and very recently with paramagnetic Cu^{II}.[5-8]

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Here, we report the design and the magnetic behavior of a trinuclear Ni(II) complex **1** containing the bridging trisemiquinone derivative HHTP^{3-}. In order to reach the most stable thermodynamic state for the bridging ligand, we carried out the preparation of the complex under aerobic conditions by mixing the mononuclear Ni[BH(TP^{Ph,Ph})$_3$]Cl, here [BH(TP^{Ph,Ph})$_3$] is Tris(3,5-diphenyl-1H-pyrazol-1-yl)(hydrido)borate[9] with H$_6$HHTP that was deprotonated six times. Elemental analysis is consistent with a neutral complex containing one HHTP and three [Ni[BH(TP^{Ph,Ph})$_3$] species (see SI for details). Assuming that Ni remained in its +II oxidation state and knowing that the capping ligand is negatively charged, the bridging ligand is, therefore, triply negatively charged (HHTP^{3-}) and is in the [sq-sq-sq] state. It has, thus, undergone a three-electron oxidation during the synthetic process.
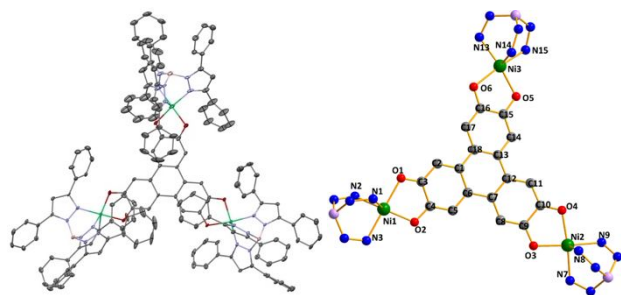

Figure 1. An ORTEP drawing of compound **1**. Hydrogen atoms and solvent molecules are omitted for clarity. Only one position of the disordered benzene moieties is shown. Thermal ellipsoids are shown at the 30% level

The crystal structure of **1** shows the formation of a trinuclear complex (Figure 1 and Figure S1). The three metal ions have a pentacoordinate coordination sphere with two (Ni2 and Ni3) in a distorted square pyramidal (*pseudo-*spy) geometry, and one (Ni1) is close to trigonal bipyramidal (*pseudo-*tbp) (Figure S1 and Table 1). The values of the C-O and C-C bonds around the three Ni atoms are in line with a semiquinone character (Table S2).[10-12]{Pierpont, 1981 #55;{Lynch, 1981 #57}Benelli, 1988

#52;Benelli, 1990 #47;Caneschi, 2002 #48} The comparison of the difference between the two C–O bond distances in the coordination sphere of each metal ion and then this difference among the three metal ions may give information on how the semiquinone character is more or less pronounced for three metal ions. Furthermore, the comparison of the OC–CO bond lengths of the benzene rings around the three metal ions can also give the same information. Indeed, ——tThe differencedifferences between the C-—O bond distances is much larger (0.053±0.014 Å) around Ni1 (*pseudo*-that has a -tbp geometry) than around Ni2 and Ni3 (less than 0.01 Å). Also, the C-C bond length is larger (1.469 Å) around Ni1 than around the other two metal ions (1.459 and 1.448 Å). The difference between the Ni1-—O bond distances (0.080±0.0107 Å) is larger than between Ni2-—O and Ni3-—O (0.026±0.013 Å). These characteristics are consistent with a more pronounced semiquinone character that seems to be localized in the coordination sphere of the *pseudo*-tbp Ni1 than for the *pseudo*-spy Ni2 and Ni3. These structural characteristics lead to the conclusion that the semiquinone *electronic* density in the vicinity of Ni1 is more localized on the OCCO group than in the vicinity of Ni2 and Ni3 where it is more delocalized towards the central ring of HHTP[3-], while around Ni2 and Ni3, the electron density would be more delocalized. Because the three semiquinone electrons belong to a highly conjugated ligand (HHTP[3-]), the three single electrons are expected to undergo a very large antiferromagnetic coupling leading to a doublet ground state ($S = \frac{1}{2}$) well separated from the other excited doublet and quartet states, so that the magnetic properties of the ligand can safely be described as a $S = \frac{1}{2}$ below room temperature. This is in contrast to the bis-bidentate-bissemiquinone and the tris-bidentate-trissemiquinone ligands reported by Dei and coworkers where conjugation is very weak leading to a weak ferromagnetic coupling between the three semiquinone electrons.[13, 14 5, 6]

Cyclic voltammetry study gives information on the relative stability of the different species (Figure 2). The rest potential is at +0.01 V vs. SCE (Saturated Calomel Electrode). Scanning towards negative potential leads to three reversible reduction waves at -0.28, -0.78 and -1.17 V vs. SCE. The pristine species is, therefore, in the [sq-sq-sq][3-] state and the three reversible waves correspond formally to the [sq-sq-sq][3-]/[cat-sq-sq][4-], [cat-sq-sq][4-]/[cat-cat-sq][5-] and [cat-cat-sq][5-]/[cat-cat-cat][6-] couples. When the potential swiped towards more positive values, only one reversible oxidation wave corresponding to the formation of the [sq-sq-q][2-] is observed (Figure S2). The reversibility of the three reduction waves indicates that no major chemical (bond formation or cleavage) or structural (coordination geometry) changes are induced by these redox processes. The comproportionation constants corresponding to the successive reduction processes were found equal to 3.48×10^8 and 4.6×10^6 indicating a less delocalized character of the [cat-cat-sq][5-] species. The stable [sq-sq-sq][3-] was already observed with Ru[II] metal ions and very recently with Cu[II] containing complexes, while for the trinuclear Co[III] complex, the bridging ligand was found to be in the [cat-cat-sq][5-] state.
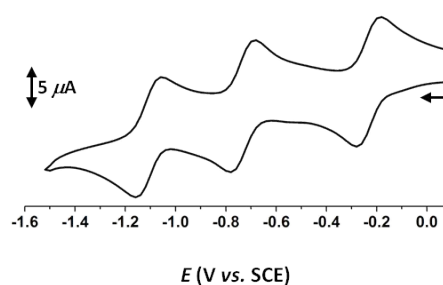

Figure 2. Cyclic voltammogram of 1mM **1** in argon-degassed dichloromethane containing 0.1 M [Bu$_4$N]PF$_6$ at 25 °C and recorded using a glassy carbon working electrode, a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

Magnetic studies allow getting insight into the interaction between the ligand centered single electron spin $S = 1/2$ and the metal centers and may thus give information on the electronic and spin delocalization. The dc magnetic measurements were carried out at 0.1 T in the 300-2 K temperature range and at T = 2, 4, 6 and 8 K between 0 and 6 T. Upon cooling, $\chi_M T$ decreases in a steady manner from 300 to 50 K and then more abruptly. It reaches a value of 0.9 cm^{3}Kmol^{-1} at 2 K, indicating the presence of dominating overall an antiferromagnetic coupling and a non-zero spin ground state (Figure 3). The magnetization versus field curves are typical of a paramagnetic ground state with large zero-field splitting (ZFS) because the $M = f(B/T)$ curves are not superimposable (Figure S3). The magnetization value at 2 K and 6 T (2.4 Bohr Magneton) is much lower than the expected values for three Ni[II] complexes and one S = 1/2 radical even considering large ZFS for Ni[II]. These results indicate the presence of a large antiferromagnetic coupling within the complex. Due to the large separation between the metal ions belonging to different molecules (13 Å) and the absence of a H-bond network, a magnetic intermolecular interaction at T > 2 K can be discarded. Also, since the intramolecular metal-metal distance is large (10 Å), the large antiferromagnetic coupling cannot be due to intramolecular direct Ni-Ni interaction. In order to fit the magnetic data, we restricted the ZFS values of the different Ni[II] species to be positive for the *pseudo*-spy geometry (Ni2 and Ni3; within the 20 - 30 cm^{-1} range) and negative for the *pseudo*--tbp species (Ni1; within the −20 - −30 range) as expected based on previous studies.[15-18] We carriedThe simultaneous fit of $\chi_M T$ and magnetization was done using the PHI software,[19] withand the following spin Hamiltonian, where we assumed that a central S = ½ radical exchange couples with three S = 1 Ni[II] species:

$$H = -J_1 S_{rad}.S_{Ni1} - J_2 S_{rad}.S_{Ni2} - J_3 S_{rad}.S_{Ni3} + D_1 S_{zNi1}^2 + D_2 S_{zNi2}^2 + D_3 S_{zNi3}^2$$

Despite the presence of two Ni(II) with similar *pseudo* square pyramidal geometry, two different coupling parameters must be considered because the trinuclear complex has no symmetry plane and the central ligand is distorted so there is no physical reason to have exactly the same coupling parameters.
The best fit parameters are leads to the following values: J_1 = -112 ± 10.6 cm^{-1}, J_2 = 11 ±5.4 cm^{-1}, J_3 = -27 ± 7.6 cm^{-1}, D_1 = -23 ± 2.6 cm^{-1}, D_2 = 26 ± 3.6 cm^{-1} and D_3 = 20 ±3.0 cm^{-1}; TIP = 4×10^{-3} (see SI). The *g*-factors were found equal to 2.14, 2.10 and 2.35

for Ni1, Ni2 and Ni3 respectively. We performed simulation of the data and found that a range of parameters give reasonable agreement with the experimental ones leading to a range of values for the parameters given by the uncertainties values above. Trials with both J_2 and J_3 ferromagnetic or antiferromagnetic may give reasonable agreement with the experimental data but with very different D_2 and D_3 which is not physically sound since the geometry around Ni2 and Ni3 is very close. While exchange coupling between octahedral Ni(II) and semiquinone species is established to be strongly ferromagnetic,[12] the coupling in the case of pentacoordinate[20-22] (for both distorted spy[20] and tbp[21][19, 20] geometries) Ni(II) complexes was found to be strongly antiferromagnetic.[20-22] Importantly, it has also been shown that the magnitude of the octahedral Ni(II)-semiquinone ferromagnetic coupling decreases when bis-semiquinone or tris-semiquinone ligands bridge two and three Ni(II) complexes,[13, 14] in comparison to the case of terminal semiquinone where the coupling is very strong. This can be attributed to the delocalization of the semiquinone single electrons on the central bridge. In our case, the central HHTP[3-] bridging ligand being highly conjugated, a larger delocalization and, hence, a decrease of the magnitude of the exchange coupling is expected in comparison to the cases where semiquinone is terminal,[12, 20, 21] therefore, justifying our results. Furthermore, the fact that J_2 and J_3 are different is not surprising because the HHTP[3-] central ligand is distorted and there is no physical reason for the orbital wave function describing the $S = 1/2$ to have exactly the same weight close to Ni2 and Ni3. [19, 20] ~~These results indicate that the radical undergoes coupling with different magnitudes and nature with the metal ions suggesting a relative delocalization over the ligand π skeleton.~~ A knowledge of the nature of the ground state wavefunction is necessary to get insight into the electronic and spin densities distribution and confirm our hypothesis; theoretical calculations are underway to do so but this is out of the scope of this communication.
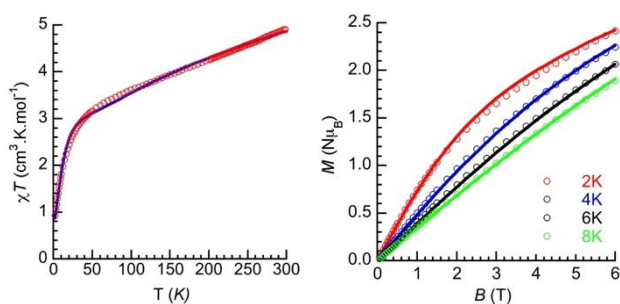

Figure 3. $\chi T = f(T)$ (top) and $M = f(B)$ (bottom) for **1**; continuous lines correspond to the best fit with parameters in the text

In order to probe the electron delocalization in the reduced species, we recorded the X-band Electron Paramagnetic Resonance (EPR) spectra (perpendicular mode) of the pristine and the three reduced species on solutions obtained by preparative reduction of the sample at -0.53 V ([(LNi)$_3$(cat-sq-sq)]$^-$), -0.98 V ([(LNi)$_3$(cat-cat-sq)]$^{2-}$) and -1.4 V ([(LNi)$_3$(cat-cat-cat)]$^{3-}$). The spectra (Figure S4 and Figure 4) show that the

pristine and the two-electron reduced species present EPR signals, while no signal is observed for the one and the three-electron reduced species. The absence of an EPR signal is due to the closed shell nature of the bridging ligand and to the fact that isolated Ni^{II} (d^8, S = 1) complexes are EPR silent in X-band perpendicular mode because of their large ZFS in comparison to the photon incident energy ($h\nu$ = 0.3 cm^{-1}). The spectrum of the pristine complex is not intense and observed only below 10 K (Figure S4); it has several bands indicative of the presence of many low-lying states coming from the interaction between the single electron and more than one Ni^{II} confirming in a qualitative manner the magnetic data. Fitting such complex spectrum to obtain more quantitative information is out of scope of this paper. The spectra of the two-electron reduced species is completely different and much simpler; it corresponds to a typical S = ½ powder EPR spectra with rhombic g anisotropy. It can be due to the coupling between a single electron localized on the [cat-cat-sq]$^{5-}$ central species and only one Ni^{II} ion. The spectrum was first simulated considering $S = ½$ species with the following g_{eff} values g_{xeff} = 2.3499, g_{yeff} = 2.2205, g_{xeff} = 2.0293 (Figure S5). The g_{eff} values are consistent with resonances belonging to a $S = ½$ species coming from an *antiferromagnetic* coupling between $S = 1$ and $S = ½$ species; the g_{eff} values for an effective spin $S_{eff} = ½$ due to a ferromagnetic coupling between a $S = 1$ and a $S = ½$ are completely different from those observed.[23]

It is possible, then, to use the relationship between g_{eff} and the local g_{rad} and g_{Ni} values ($g_{eff} = -g_{rad}/3 + 4g_{Ni}/3$) to compute the g_{Ni} components assuming g_{rag} = 2.000. We obtain g_{xNi} = 2.022, g_{yNi} = 2.1650 and g_{zNi} = 2.2622 with g_{avNi} = 2.15 consistent for a Ni(II) square pyramidal geometry.[24] The final step consisted in simulating the experimental spectrum by fixing the g_{iNi} values, fixing a negative value for J and changing the D_{Ni} value. The best calculated spectrum gives a positive D_{Ni} value and a $|J|/D = 20$ (the spectra depend only on $|J|/D$). Negative D values fail to reproduce the exact resonances for any J/D ratio. This analysis leads to the conclusion that in the two-reduced species, the central ligand electronic density is strongly antiferromagnetically coupled to one of the Ni(II) ions possessing the distorted *square pyramidal* geometry. Since the D value for *pseudo*-spy Ni(II) geometry is larger than 20 cm^{-1}, the exchange parameter coupling is, therefore, larger (in absolute value) than 400 cm^{-1} consistent with the literature.[20]

~~The fit of the spectrum leads to the following values: g_{rad} = 2.000, g_{xNi} = 2.022, g_{yNi} = 2.154, g_{zNi} = 2.265; J_{radNi} and D_{Ni} were set to = -200 and 20 cm^{-1} respectively. The spectra are independent from the ratio J/D, and the relative intensities of the bands are better reproduced with positive D values.[22] The g values are typical for Ni^{II} complexes with distorted geometry.~~
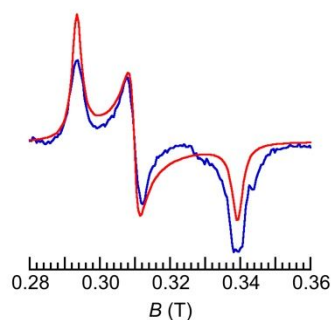
Figure 4. EPR spectra of two-electron reduced **1** in dichloromethane solution (blue) and the calculated spectrum (red) with the parameters in the text (microwave power = 1 mW, modulation amplitude = 8 Gauss, gain = 50 db, temperature = 30 K).

In conclusion, the electronic density of the trissemiquinone central ligand is relatively strongly antiferromagnetically coupled to the *pseudo*-tbp Ni(II) (Ni1) moiety and weakly coupled to the other two Ni(II) in the pristine species, while in the two-reduced species, it is very strongly coupled to one of the *pseudo*-spy Ni(II) (Ni2 or Ni3) ions evidencing an electron transfer from one side of the molecule to another upon reduction. Wwe have evidenced that Ni$_3$HHTP can be reversibly switched between different oxidation states of distinct magnetic properties that can, eventually, be addressed by an electrical field, evidencing, therefore, their potential to be used for the design of quantum devices. HHTP and related bridging ligands containing nitrogen and sulfur instead of oxygen have been used during the last five years for the development of original two-dimensional (2D) coordination networks with paramagnetic ions presenting unique conducting properties and that can be used as sensors and/or for catalysis.[25-31] Beyond the interest in electrically switchable discrete magnetic molecular complexes, investigating their electronic behavior may bring new insights and help understanding the synergy between the magnetic and the conducting properties of the 2D extended networks.

Acknowledgement

Conflicts of interest

There are no conflicts to declare.

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Supporting Information

Electronic and spin delocalization in a switchable trinuclear triphenylene trisemiquinone bridged Ni$_3$ complex

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Keywords: triphenylene, trisemiquinone, switchable, Ni, HHTP

I-Synthesis and characterization

KBH(TP^{Ph,Ph})$_3$ (1.89 g, 2.7 mmol) was dissolved in 60 mL CHCl$_3$, and the colorless solution was added into a methanolic solution of NiCl$_2$·6H$_2$O (0.71 g, 3 mmol) with stirring. A pink precipitate was generated immediately. Two hours later, the solid was filtered, washed with a small amount of CHCl$_3$ and dried under vacuum. The pink solid obtained corresponds to Ni[BH(TP^{Ph,Ph})$_3$]Cl.

HHTP (32.5 mg, 0.01 mmol) was dissolved in a methanolic solution (15 mL) containing 0.6 mL of tetrabutylammonium hydroxide (TBAOH). The obtained dark violet solution was added to a 15 mL CH$_2$Cl$_2$ solution of Ni[BH(TP^{Ph,Ph})$_3$]Cl (229 mg, 0.3 mmol) with stirring. A darkish blue suspension was produced. The reaction was left overnight, and then filtered. A black precipitate was obtained, it was thoroughly washed with methanol. Yield 62%, 156 mg. The solid was redissolved in CHCl$_3$, and the final solution was obtained after chromatography (SiO$_2$). The solvent was completely removed using a rotatory evaporator. The solid obtained was dissolved in acetone and crystals suitable for X-ray analysis were obtained by slowly evaporating acetone. Elem Anal. for Ni$_3$(HHTP)[BH(TP^{Ph,Ph})$_3$]$_3$(C$_3$H$_6$O)$_{0.5}$ Calcd: C, 73.19%; H, 4.53%; N, 9.94%; Found: C, 73.14%; H, 4.35%; N, 10.04%. M$_W$ = 2535.19 g/mol. Single-crystal unit cell: Triclinic, space group, P-1. a = 14.2552(18) Å, b = 17.287(2) Å, c = 32.407(4) Å, α = 94.408(4)°, β = 101.051(4)°, γ = 101.473(4)°, V = 7626.4(17) Å^3. IR (KBr) v/cm^{-1}: 3456 (w), 3062 (w), 2617 (w), 1603 (w), 1545 (s), 1502 (s), 1479 (s), 1462 (s), 1364 (m), 1329 (m), 1282 (w), 1232 (w), 1170 (m), 1118 (w), 1064 (m), 1013 (m), 972 (w), 915 (w), 844 (w), 827 (w), 803 (s), 759 (s), 696 (s), 669 (m), 619 (w), 571 (m), 543 (m), 403 (w), 353 (w).

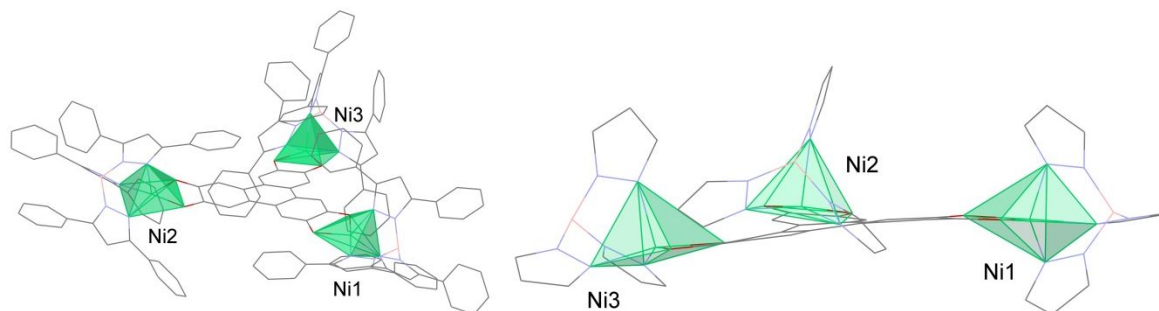## II-Single Crystal X-ray analysis

Figure S1. Polyhedral representation of the crystal structure

X-ray diffraction data for compound **1** was collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IuS source Mo Kα radiation. Crystal was mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value by means of an N-Helix to within an accuracy of ±1K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[2] with anisotropic displacement parameters for all non-hydrogen atoms. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.[3]

The crystal data collection and refinement parameters are given in Table S1.

CCDC 1936818 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure.

Table S1. Crystallographic data and structure refinement details.

Compound	1
CCDC	1936818
Empirical Formula	$C_{153} H_{108} B_3 N_{18} Ni_3 O_6, 7(C_3 H_6 O)$
M_r	2909.67
Crystal color	black
Crystal size, mm^3	0.100 x 0.095 x 0.035
Crystal system	triclinic
Space group	P -1
a, Å	14.2552(18)
b, Å	17.287(2)
c, Å	32.407(4)

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α, °	94.408(4)
β, °	101.051(4)
γ, °	101.473(4)
Cell volume, Å^3	7626.4(17)
Z ; Z′	2 ; 1
T, K	100 (1)
Radiation type ; wavelength Å	MoKα; 0.71073
F$_{000}$	3046
μ, mm^{-1}	0.435
θ range, °	2.156 - 30.951
Reflection collected	217 860
Reflections unique	47 603
R$_{int}$	0.3232
GOF	1.015
Refl. obs. ($I>2\sigma(I)$)	16 901
Parameters	1856
wR$_2$ (all data)	0.3393
R value ($I>2\sigma(I)$)	0.1390
Largest diff. peak and hole (e-.Å^{-3})	1.483 ; -1.004

Table S2. Some selected bonds distances and angles of complex

Complex					
Ni1		Ni2		Ni3	
d_{Ni1-N1}	2.009(5)	d_{Ni2-N7}	2.057(6)	$d_{Ni3-N13}$	2.038(5)
d_{Ni1-N2}	1.987(5)	d_{Ni2-N8}	2.031(7)	$d_{Ni3-N14}$	2.018(5)
d_{Ni1-N3}	2.067(5)	d_{Ni2-N9}	2.040(7)	$d_{Ni3-N15}$	2.028(5)
d_{Ni1-O1}	2.039(4)	d_{Ni2-O3}	1.984(6)	d_{Ni3-O5}	1.971(4)
d_{Ni1-O2}	1.957(5)	d_{Ni2-O4}	2.020(5)	d_{Ni3-O6}	2.022(4)
d_{C3-O1}	1.247(7)	d_{C9-O3}	1.293(9)	d_{C15-O5}	1.291(7)
d_{C4-O2}	1.300(7)	d_{C10-O4}	1.270(8)	d_{C16-O6}	1.278(7)
d_{C3-C4}	1.469(8)	d_{C9-C10}	1.459(10)	$d_{C15-C16}$	1.448(9)
$\widehat{O1Ni1O2}$	81.94(17)	$\widehat{O3Ni2O4}$	81.8(2)	$\widehat{O5Ni3O6}$	81.92(17)

III-Electrochemical Characterization Procedures

Cyclic voltammetry measurements were performed in an electrochemical cell composed of a glassy carbon (3 mm diameter) working electrode, a saturated calomel electrode (SCE) as a reference electrode and a platinum mesh counter electrode. Dichloromethane (Fisher Chemical 99+%) was distilled over $CaCl_2$ and *tetra-N*-butylammonium hexafluorophosphate ($[Bu_4N]PF_6$, Aldrich 99%) was recrystallized in ethanol. Solutions of the complex were prepared at a concentration of 1 mM and $[Bu_4N]PF_6$ was used as supporting electrolyte and its concentration was maintained at a hundred-fold excess compared to the sample. The solutions were purged with inert argon gas and the cyclic voltammograms were measured at a scan rate of 100 mV/s.
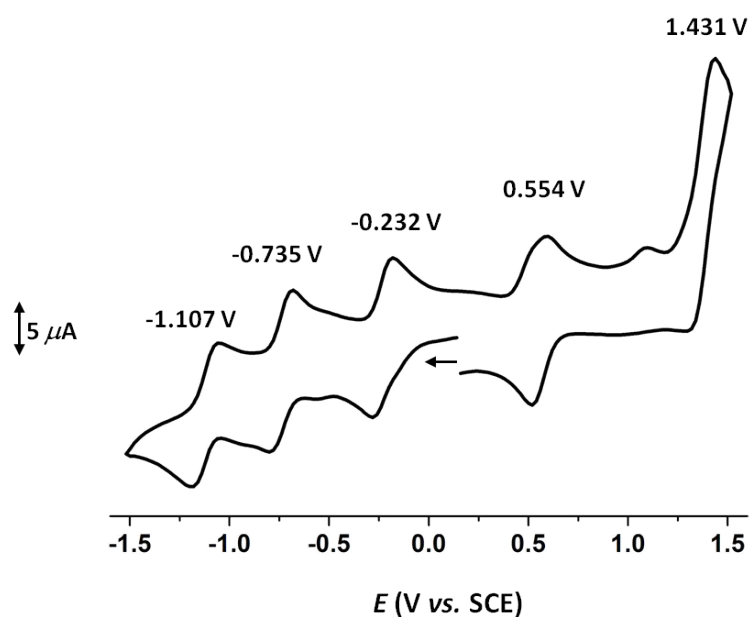

Figure S2. Cyclic voltammograms of 1mM **1** in argon-degassed dichloromethane containing 0.1 M $[Bu_4N]PF_6$ at 25 °C and recorded using a glassy carbon working electrode, a platinum mesh as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

Bulk electrolysis for the preparation of the samples for EPR studies was performed in the same conditions as for cyclic voltammetry experiments except for the glassy carbon working electrode that was replaced by 5 mm³ carbon foam with high effective surface (Alfa Aesar. carbon felt 99.0%). After each electrolysis, samples were transferred using a cannula under argon atmosphere into EPR tubes and then frozen immediately in a liquid nitrogen bath.
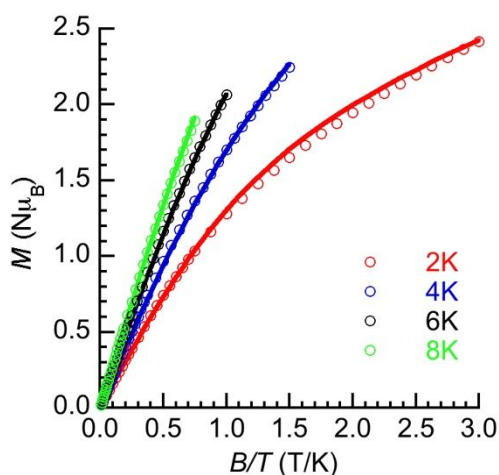
IV-Magnetic studies

Figure S3. M = f(*B/T*) for **1**.

The magnetic data were fitted by fixing the rhombic parameters *E* for the three Ni^{II} to zero. Letting the *E* values free during the fitting procedure does not lead to a large change in the axial ZFS parameters *D*; the *J* values are also not very different. The best fit solution is not unique. Other solutions can be found by interchanging the *J* values; they however remain in the same range: one strongly antiferromagnetic, one weakly antiferromagnetic and weakly ferromagnetic. ~~Furthermore, one solution that have a good agreement with the magnetic experimental data with one very strong antiferromagnetic coupling (-800 cm^{-1}) and two extremely weak coupling (few cm^{-1}) was also found. However, this solution leads to ground state with S = ½ very separated from the excited states, which does not correspond to the EPR data. This solution was discarded.~~

V-Electron Paramagnetic Resonance

X-band EPR spectra were recorded on a Bruker ELEXSYS 500 spectrometer equipped with a Bruker ER 4116DM X band resonator, an Oxford Instrument continuous flow ESR 900 cryostat, and an Oxford ITC 503 temperature control system.
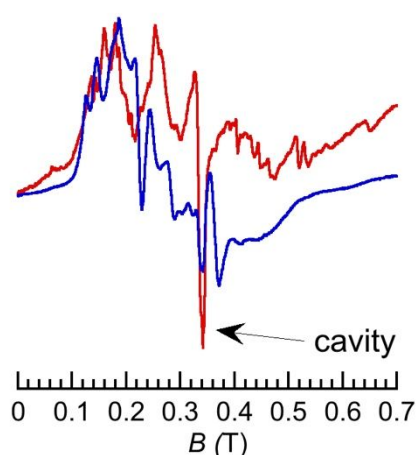

Figure S4. EPR spectra of **1** in dichloromethane solution (blue) and the solid state (red) at T = 5 K

(Microwave power = 1 mW, modulation amplitude = 8 Gauss, gain = 50 db, temperature = 5 K).
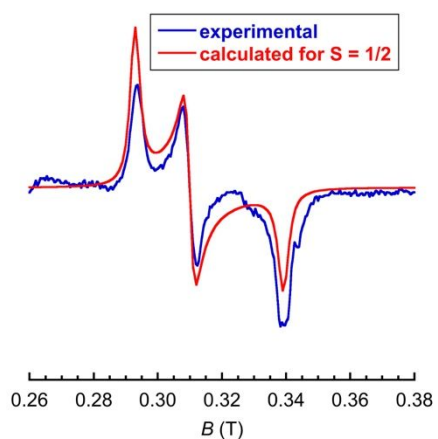

Figure S5. EPR spectra of the two-reduced species (blue) ((microwave power = 1 mW, modulation amplitude = 8 Gauss, gain = 50 db, temperature = 30 K) and simulation (red) considering S = ½ with the following g_{eff} values g_{xeff} = 2.3499, g_{yeff} = 2.2205, g_{xeff} = 2.0293

Electronic and spin delocalization in a switchable trinuclear triphenylene trisemiquinone bridged Ni$_3$ complex

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Table of Contents

An electro- switchable trinuclear Ni$_3$-trisemquinone complex with electronic and spin dependent oxidation state delocalization