

The redox effect of the $[1,2-(\text{NH})_2\text{C}_6\text{H}_4]^{2-}$ ligand in the formation of transition metal compounds

Francesca A. Stokes, Lars Kloo, Yaokang Lv, Philip J. Harford,
Andrew E. H. Wheatley* and Dominic S. Wright*

^a Chemistry Department, Cambridge University, Lensfield Rd, Cambridge CB2 1EW (U.K.); e-mail
aehw2@cam.ac.uk, dsw1000@cam.ac.uk.

^b Department of Chemistry, Royal Institute of Technology, Teknikringen 36, S-100 44,
Stockholm (Sweden); e-mail larsa@kth.se.

Synthesis and characterisation

General synthetic and analytical details

Reagents were purchased from Sigma Aldrich and used without further purification. Reactions and manipulations were carried out under an inert atmosphere of dry argon, using standard double manifold and glove-box techniques. Cp_2M (M = V, Mn) was prepared by a modified literature method. Cyclopentadiene was cracked immediately prior to use. 1,2-benzenediamine was stored over 4 Å molecular sieve and then distilled prior to use. THF was distilled off sodium-potassium amalgam immediately before use. NMR data were collected on a Bruker DRX 500 FT NMR spectrometer (500.05 MHz for ^1H , 125.8 MHz for ^{13}C). All spectra were obtained at 27 °C and chemical shifts are internally referenced to d_6 -DMSO and calculated relative to TMS. Chemical shifts are expressed in δ ppm. The following abbreviations are used for NMR spectra: s = singlet, m = multiplet.

General crystallographic details

Data collected using the 'oil drop technique'¹ to mount crystals on a Nonius Kappa-CCD equipped with an Oxford Cryostream low-temperature device. Structures solved by direct methods,² with refinement on F^2 , by full-matrix least squares.³ Non-H atoms refined anisotropically and a riding model employed for H-atoms. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 892665 and 892666. Copies obtainable free of charge from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Synthesis of **1**

Freshly sublimed 1,2-benzenediamine (90 mg, 0.83 mmol) was dissolved in 5 ml of THF. $^n\text{BuLi}$ (1.0 ml, 1.6 mol L^{-1} in hexanes, 1.60 mmol) was syringed into this solution dropwise under Ar at -78 °C. A solution of Cp_2V^4 (100 mg, 0.55 mmol) in 5 ml THF was cooled to -78°C and added dropwise by syringe. The resulting dark solutions were allowed to warm to room temperature. They were stirred overnight before being filtered warm through Celite. Storage at room temperature afforded highly air-sensitive green crystals of **1** in a dark green solution. Yield 75 mg (36 % with respect to Cp_2V). ^1H NMR (500.05 MHz, d_6 -DMSO), δ (ppm) = 6.47 (6H, m, HNCH), 6.34 (6H, m, HNCHCH), 5.30 (5H, s, C_5H_5), 4.36 (6H, s, NH), 3.58 (16H, m, THF CH_2O),

Crystal data for **1**

$C_{39}H_{55}LiN_6O_4V_2$, $M = 780.71$, monoclinic, space group $P2_1/c$, $Z = 4$, $a = 15.3041(1)$, $b = 20.2762(3)$, $c = 13.8669(2)$ Å, $\beta = 114.35(3)^\circ$, $V = 3920(1)$ Å³, $\mu(\text{Mo-K}\alpha) = 0.524$ mm⁻¹, $\rho_{\text{calc}} = 1.323$ Mg m⁻³, $T = 180(2)$ K. Total reflections 34260, unique 11221 ($R_{\text{int}} = 0.040$). $R1 = 0.049$ [$I > 2\sigma(I)$] and $wR2 = 0.172$ (all data).

Computational data for **1**

Calculations were done using Gaussian09 and the cam-B3LYP hybrid exchange-correlation functional including corrections for long-range interactions. Lighter elements used 6-311G-type basis sets supplemented with diffuse and polarization functions. An MDF10 effective core potential and a (8s7p6d1f)/[6s5p3d1f] valence space for V.^{5,6,7} The symmetry of the monoanion of **1** derived from the crystal structure was close to C_s . This symmetry was used in most calculations with final optimizations of the higher spin states allowed to deviate into formal C_1 symmetry. An Atoms in Molecules (AIM) analysis was used to display a bond critical point midway between the two V atoms.⁸

In order to probe the nature of the V...V interaction in **1** further, a quantum chemical study of the anion was undertaken. This was made relatively complex by the different possible spin states. Formally, the monoanion contains two V atoms in the +3 oxidation state, each having two valence d-electrons. All of the possible closed-shell singlet state, the triplet and the pentet states, as well as open-shell singlet states derived from anti-ferromagnetic coupling of the non-paired electrons in the singlet, triplet and pentet states were investigated using the multistep broken symmetry procedures recommended by Gaussian, Inc. The multistep procedure involves a search for more stable configurations within the spin state (allowing anti-ferromagnetic coupling), subsequent geometry optimization and finally an FMO analysis. Calculations used the cam-B3LYP hybrid exchange-correlation functional including corrections for long-range interactions with 6-311G-type basis sets supplemented with diffuse and polarization functions for lighter atoms and an MDF10 effective core potential and a (8s7p6d1f)/[6s5p3d1f] valence space for V.⁵⁻⁶ The Gaussian09 keywords used for the basis set were '6-311G+G(d,p)' for the light elements and the combination of 'SDD' and 'MDF10' for V. The symmetry of the monoanion of **1** derived from the crystal structure was close to C_s . This symmetry was used in most calculations with final optimizations of the higher spin states allowed to deviate into formal C_1 symmetry. However, in pursuing the broken symmetry searches, typically all symmetry requirements were cancelled and the final optimized structure formally belongs to the C_1 point group. The main difference between structures optimized within C_s and C_1 is that the axially coordinated LH_2^{2-} ligand twists out of the imposed mirror plane and that the bond distances to the donating N-atoms of the equatorial LH_2^{2-} ligands differ slightly.

The closed-shell singlet state offered the best correlation with experimentally-observed structure, bond lengths and magnetic behaviour. However, optimization of the open-shell pentet state (maximum spin state of the compound) using a broken symmetry approach converged to an open-shell singlet state with the lowest observed total energy for the system studied. At the level of calculation used, the anti-ferromagnetically coupled open-shell singlet within the pentet electronic state was as much as 206 kJ mol⁻¹ lower in energy (more stable) than the closed-shell singlet state in C_s symmetry and 190 kJ mol⁻¹ lower in energy than the one in formal C_1 symmetry. However, the resulting spins on the two V atoms was 2 (in an FMO analysis the spins were 2.04 and 2.08, respectively), and the V-V distance as long as 2.622 Å. Calculations on the open-shell singlet and triplet states strived towards the same open-shell singlet state and were not pursued to a final analysis.

The open-shell singlet state

The coordinates and image of the structurally optimized open-shell singlet is given below in Table S1 and Fig. S3, respectively.

Table S1. The coordinates of the structurally optimized monoanion of **1** in the open-shell singlet state (C_1 symmetry).

Element	x / Å	y / Å	z / Å
V	1.84383600	0.00544700	0.00225200
V	-0.77795200	0.00145200	0.00048100
N	0.55712600	1.24262400	1.19834800
H	0.50592300	1.15831100	2.20622700
N	0.76878900	1.34190600	-1.19282300
H	0.80493400	1.32727400	-2.20417500
N	-2.27843800	1.16206000	-0.47398200
H	-2.25898900	2.10906600	-0.83196600
N	-2.27458800	-1.16471500	0.47407500
H	-2.25185300	-2.11131700	0.83291900
N	0.56041500	-1.23655100	-1.19747300
H	0.50827000	-1.15203100	-2.20531400
N	0.77155600	-1.33594600	1.19367000
H	0.81020300	-1.32148500	2.20504200
C	3.85862200	-1.06587800	0.56342900
H	3.81518700	-2.02004400	1.06616600
C	3.83966300	0.20545600	1.18101800
H	3.80374800	0.39498200	2.24341000
C	3.83999400	1.18603800	0.16379100
H	3.78588700	2.25470100	0.30829700
C	3.85641500	0.51695900	-1.08057100
H	3.82677500	0.99034500	-2.05013100
C	3.87092200	-0.87318500	-0.83310100
H	3.84478800	-1.65550500	-1.57668400
C	0.59075400	2.56869700	0.75504200
C	0.51412800	3.73478700	1.48838800
H	0.40962000	3.69002400	2.56801700
C	0.55466100	4.97570800	0.83210200
H	0.49201100	5.89039000	1.41081000
C	0.66549300	5.02923100	-0.54335600
H	0.69175600	5.98752900	-1.05037400
C	0.74542600	3.84673000	-1.29535400
H	0.83280500	3.89053400	-2.37667200
C	0.71311800	2.62036900	-0.65504800
C	-3.54164300	0.65669200	-0.26699000
C	-4.75682100	1.28884600	-0.51522000
H	-4.75562700	2.29876500	-0.91590500
C	-5.96449100	0.63709400	-0.25711300
H	-6.90273200	1.14338100	-0.45813000
C	-5.96228900	-0.65406000	0.25259500
H	-6.89880300	-1.16400400	0.45244100
C	-4.75245200	-1.30113900	0.51220500
H	-4.74782900	-2.31105100	0.91287600
C	-3.53939400	-0.66429400	0.26544800
C	0.59468900	-2.56263000	-0.75449000
C	0.51759500	-3.72866100	-1.48773300
H	0.41262400	-3.68394600	-2.56734300
C	0.55715200	-4.96974500	-0.83132300
H	0.49414700	-5.88435400	-1.41012000
C	0.66764100	-5.02340300	0.54390600
H	0.69313700	-5.98168800	1.05099400
C	0.74809000	-3.84071100	1.29604900
H	0.83373400	-3.88455500	2.37755300
C	0.71620000	-2.61450800	0.65574700

V	1.84383600	0.00544700	0.00225200
V	-0.77795200	0.00145200	0.00048100

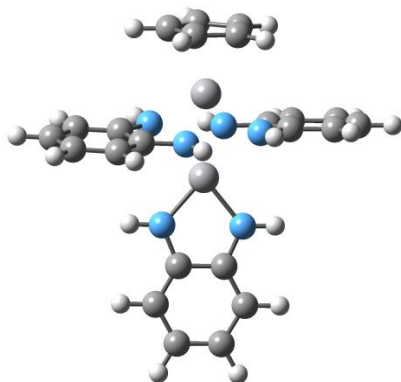


Fig. S3. A view of the structurally optimized monoanion of **1** in the open-shell singlet state (C_1 symmetry).

It is notable that the V-V distance is as long as 2.622 Å in this structure, and this is one of the key features that render the open-shell singlet structure as non-feasible. In spite of the fact that it from a purely calculational point of view represents the lowest observed total energy and thus should be regarded as the most stable, *i.e.* most likely, state and structure of the monoanion of **1**. The coordinates and image of the structurally optimized closed-shell singlet is given below in Table S2 and Fig. S4, respectively.

Table S2. The coordinates of the structurally optimized monoanion of **1** in the closed-shell singlet state (C_1 symmetry).

Element	x / Å	y / Å	z / Å
V	0.00000000	0.00000000	0.00000000
V	0.00000000	0.00000000	2.34649027
N	1.76784883	0.00000000	1.25014823
H	2.41259061	-0.77137230	1.37053132
N	0.14864342	1.76160312	1.07621971
H	-0.57977363	2.46344255	1.12622927
N	0.04346313	1.25181414	3.79734338
H	0.13057373	2.26110463	3.78239273
N	-0.03692091	-1.25105067	3.79829053
H	-0.12050461	-2.26061744	3.78479900
N	-1.76761124	0.00434659	1.25503382
H	-2.41185245	0.77618492	1.37584632
N	-0.15154683	-1.76343853	1.07198351
H	0.57369325	-2.46868148	1.12247205
C	0.01564903	-1.24328349	-2.00151073
H	0.02540150	-2.32298145	-1.99038751
C	1.14621019	-0.40901146	-1.97196520
H	2.17469162	-0.73796863	-1.96180604
C	0.70697735	0.93507639	-1.88002511
H	1.34135529	1.80703698	-1.83569875
C	-0.71998759	0.92195353	-1.85108381
H	-1.36600706	1.78535244	-1.81807415
C	-1.13595937	-0.43749485	-1.91849862
H	-2.15221873	-0.79868744	-1.86933040
C	2.39049860	1.25191769	1.26341156
C	3.73420339	1.55355882	1.34191105

H	4.46651835	0.75654527	1.42492762
C	4.14592881	2.89591366	1.32552031
H	5.20207955	3.13273469	1.38922487
C	3.21146907	3.90904122	1.23657404
H	3.53163485	4.94511474	1.22791445
C	1.84295869	3.60662815	1.15660582
H	1.10853288	4.40287931	1.08220400
C	1.43212643	2.28666592	1.16348699
C	0.03096478	0.70900930	5.07404464
C	0.06284660	1.39330664	6.27967605
H	0.10756523	2.47839150	6.27551344
C	0.03676598	0.69345001	7.49093350
H	0.06158785	1.23947730	8.42764489
C	-0.02246957	-0.68984807	7.49153005
H	-0.04588165	-1.23519878	8.42866650
C	-0.05104632	-1.39061008	6.28081721
H	-0.09614924	-2.47569413	6.27760595
C	-0.02172771	-0.70722791	5.07465753
C	-2.39284153	-1.24603555	1.25663654
C	-3.73806314	-1.54375301	1.32680015
H	-4.46777174	-0.74469140	1.41286519
C	-4.15453214	-2.88437827	1.29879275
H	-5.21185493	-3.11766609	1.35616543
C	-3.22354537	-3.90045592	1.20701794
H	-3.54743761	-4.93525359	1.18997039
C	-1.85379816	-3.60218705	1.13454520
H	-1.12184465	-4.40057165	1.05802131
C	-1.43814214	-2.28394368	1.15162505

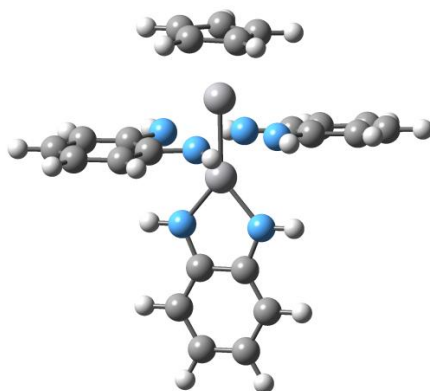


Fig. S4. A view of the structurally optimized monoanion of **1** in the closed-shell singlet state (C_1 symmetry).

The closed-shell singlet state

The simplest electronic model, the closed-shell singlet state, turns out to represent the model that describes the experimental features most closely. All atom-atom distances are close to those derived from the crystal structure analysis and it is diamagnetic.

A bonding analysis of the closed-shell singlet model involved both a topological investigation of the MOs down to at least HOMO-20, an NBO analysis utilizing the Gaussian09-implemented version of NBO v.3.1, and an AIM analysis using the AIMALL package.⁸ As noted in the main text, all indications point at a single V-V bond, where the direct mid-point between the V^{3+} -ions displays an accumulation of electron density that is very similar to those between the V- and N-atoms in the compound. There are no obvious signs of any π -type of bond

between the V^{3+} -ions. The image from AIMALL displaying all bond critical points is shown in Fig. S5. Ring and cage critical points were analysed but are not included in the figure.

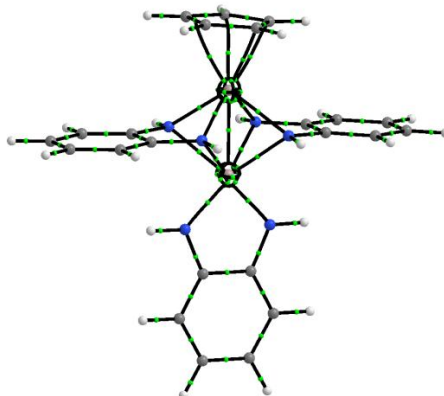
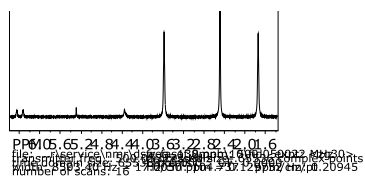


Fig. S5. A view of the bond critical points identified in the closed-shell singlet model. The green spheres represent the bond critical points and the black atom-atom connections the bond paths.

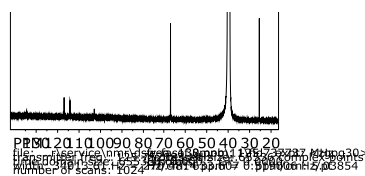
Synthesis of 2

Freshly sublimed 1,2-benzenediamine (60 mg, 0.55 mmol) was dissolved in 5 ml of THF. ${}^n\text{BuLi}$ (0.7 ml, 1.6 mol L^{-1} in hexanes, 1.10 mmol) was syringed into this solution dropwise under Ar at -78°C . A solution of Cp_2Mn^4 (100 mg, 0.55 mmol) in 5 ml THF was cooled to -78°C and added dropwise by syringe. The resulting dark solutions were allowed to warm to room temperature. They were stirred overnight before being filtered warm through Celite. Storage at room temperature afforded highly air-sensitive green crystals of **2** in a dark pink solution. Yield 45 mg (39% with respect to Cp_2Mn). ${}^1\text{H}$ NMR (500.05 MHz, d_6 -DMSO), δ (ppm) = 6.46 (12H, m, HNC H), 6.34 (12H, m, HNC HCH), 4.35 (12H, m, NH), 3.58 (60H, m, THF CH_2O), 1.74 (60H, m, THF CH_2). Paramagnetic effects on relaxation prevent meaningful comparison of the $[\text{1,2-C}_6\text{H}_4(\text{NH})_2]^{2-}$ and THF integrals.⁹ ${}^{13}\text{C}$ NMR (125.8 MHz, d_6 -DMSO) δ (ppm) = 134.9 (HNC), 117.2 (HNC CHCH), 114.5 (HNC CH), 67.0 (THF CH_2O), 25.1 (THF CH_2). Elemental analysis, found C 47.9, H 4.7, N 10.7, calcd. for **1**, C 52.4, H 6.5, N 10.8. We attribute the poor C analysis in particular to the formation of metal carbides in combustion. Despite repeated attempts we were unable to obtain more satisfactory analysis of **2**.



*

Fig. S6 ¹H NMR spectrum of **2** in *d*₆-DMSO (●). *Trace Cp.



*

Fig. S7 ¹³C NMR spectrum of **2** in *d*₆-DMSO (●). *Trace Cp.

Crystal data for 2·4THF

C₆₈H₁₀₀Mn₆N₁₂O₉, *M* = 1559.24, monoclinic, space group *P*2₁/*c*, *Z* = 2, *a* = 13.2698(2), *b* = 16.7091(3), *c* = 16.7888(3) Å, β = 101.7800(10)°, *V* = 3644.12(11) Å³, μ(Mo-Kα) = 1.070 mm⁻¹, ρ_{calc} = 1.421 Mg m⁻³, *T* = 180(2) K. Total reflections 32704, unique 6640 (*R*_{int} = 0.057). *R*1 = 0.046 [*I* > 2σ(*I*)] and *wR*2 = 0.132 (all data).

References

- 1 T. Kottke, D. Stalke, *J. Appl. Cryst.* 1993, **26**, 615.
- 2 G. M. Sheldrick, *Acta Crystallogr., Sect. A* 1990, **46**, 467.
- 3 G. M. Sheldrick, *SHELXL-97 Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.
- 4 G. Wilkinson, F. A. Cotton and J. M. Birmingham, *J. Inorg. Nucl. Chem.* 1956, **2**, 95.
- 5 Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 6 T. Yanai, D. P. Tew and N. C. Handy, *Chem. Phys. Lett.* 2004, **393**, 51.
- 7 M. Dolg, U. Wedig and H. Preuss, *J. Chem. Phys.* 1987, **86**, 866.
- 8 R. Bader, *Chem. Rev.* 1991, **91**, 893–928. AIMAll (Version 11.12.19), T. A. Keith, T. K. Gristmill Software, Overland Park KS, USA, 2011 (aim.tkgristmill.com).
- 9 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View*, Longman Scientific & Technical, Harlow, Essex, 1986, 130-131.