TETRAHEDRAL NICKEL(II) AND COBALT(II) BIS-O-IMINOBENZOSEMIQUINONATES

Irina V. Ershova, Ivan V. Smolyaninov, Artem S. Bogomyakov, Matvey V. Fedin, Andrey G. Starikov, Anton V. Cherkasov, Georgy K. Fukin, and Alexandr V. Piskunov*

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Figure S4. Optimized geometries of complex **1** and model complexes with N-*iso*-propyl substituents, calculated by the DFT UB3LYP/6-31G(d,p) method. Hydrogen atoms are omitted for clarity. The bond lengths are given in angstroms (Å) **8**

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References **13**

Table S1. Coordination geometry and electronic structure of four coordinate nickel and cobalt bis-ligand complexes with different redox active ligands

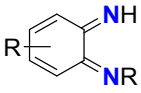
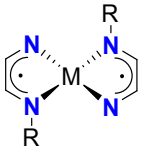
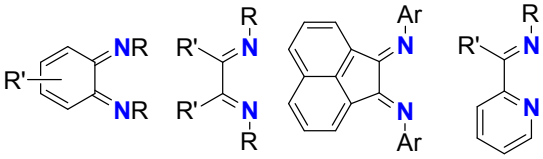
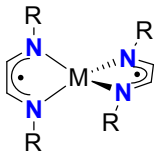
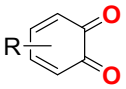
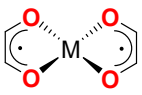
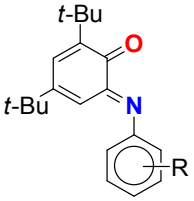
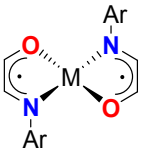
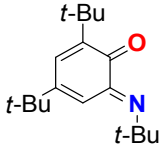
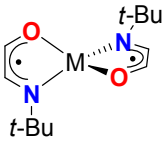
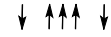
Ligand type	Coordination geometry	Electronic structure	Ref.
 *o*-diiminobenzoquinone	 $(disq)_2M$ Square planar	M = Ni^{II} (l.s.)  disq-Ni-disq (S_t = 0) M = Co^{II} (l.s.) vs Co^{III} (i.s.)  disq-Co-disq disq-Co-IP (S_t = 1/2)	1-4 1, 5, 6
 **1** **2** **3** **4** **1** *o*-diiminobenzoquinone **2** 1,4-diaza-1,3-butadiene **3** bis(arylimino)acenaphthene **4** α-iminopyridine	 $(L^-)_2M$ (L = disq, DAD, BIAN, IP) From ideal to strongly distorted tetrahedron	M = Ni^{II} (h.s.)  L^- - Ni - L^- (S_t = 0) M = Co^{II} (h.s.)  L^- - Co - L^- (S_t = 1/2)	7-20 7, 8, 10, 11, 20, 21
 *o*-benzoquinone	 $(SQ)_2M$ Square planar	M = Ni^{II} (l.s.) SQ-Ni-SQ (S_t = 0)	22, 23
 *N*-Ar-*o*-iminobenzoquinone	 $(imSQ)_2M$ Square planar	M = Ni^{II} (l.s.) imSQ-Ni-imSQ (S_t = 0) M = Co^{II} (l.s.) vs Co^{III} (i.s.)  imSQ-Co-imSQ imSQ-Co-AP (S_t = 1/2)	6, 24-29 30-33
 *N*-*t*-Bu-*o*-iminobenzoquinone	 $(imSQ)_2M$ Distorted tetrahedron	M = Ni^{II} (h.s.)  imSQ-Ni-imSQ (S_t = 0) M = Co^{II} (h.s.)  imSQ-Co-imSQ (S_t = 1/2)	This work

Table S2. Crystallographic data and structure refinement details for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{36}H_{58}NiN_2O_2$	$C_{36}H_{58}CoN_2O_2$
Formula weight	609.55	609.77
Crystal system	Triclinic	Triclinic
Space group	*P–1*	*P–1*
Unit cell dimensions		
a [Å]	10.7752(6)	10.806(3)
b [Å]	11.5077(6)	11.558(3)
c [Å]	15.6525(13)	15.589(3)
α [˚]	79.537(6)	79.570(4)
β [˚]	76.217(7)	76.133(5)
γ [˚]	72.440(5)	72.544(5)
V [Å^3]	1784.5(2)	1790.5(7)
Z	2	2
d_{calc} [g cm^{-3}]	1.134	1.131
μ [mm^{-1}]	0.574	0.510
F_{000}	664	662
Crystaldimensions [mm^3]	0.43 × 0.25 × 0.08	0.80 × 0.80 × 0.05
θ range for data collection [˚]	3.10–28.70	2.43–27.10
Reflections collected	11315	19410
Independent reflections (R_{int})	11315(R_{int} = 0.1003)	7834(R_{int} = 0.0757)
Completeness to θ [%]	99.8	99.5
Data/restraints/parameters	11315 / 0 / 389	7834 / 0 / 388
Final *R*indices [$I>2\sigma(I)$]	R_1 = 0.0741 wR_2 = 0.1450	R_1 = 0.0578 wR_2 = 0.1278
Final *R* indices (all data)	R_1 = 0.1080 wR_2 = 0.1573	R_1 = 0.0824 wR_2 = 0.1393
$S(F^2)$	1.031	1.014
Largest diff. peak and hole [e Å^{-3}]	0.95 /–0.97	1.05 /–1.03

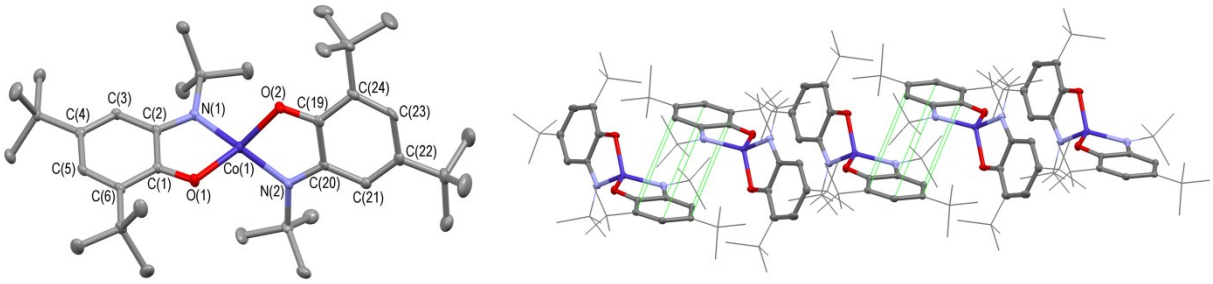


Figure S1. Molecular structure (left) and fragment of crystal packing of **2** (right). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted.

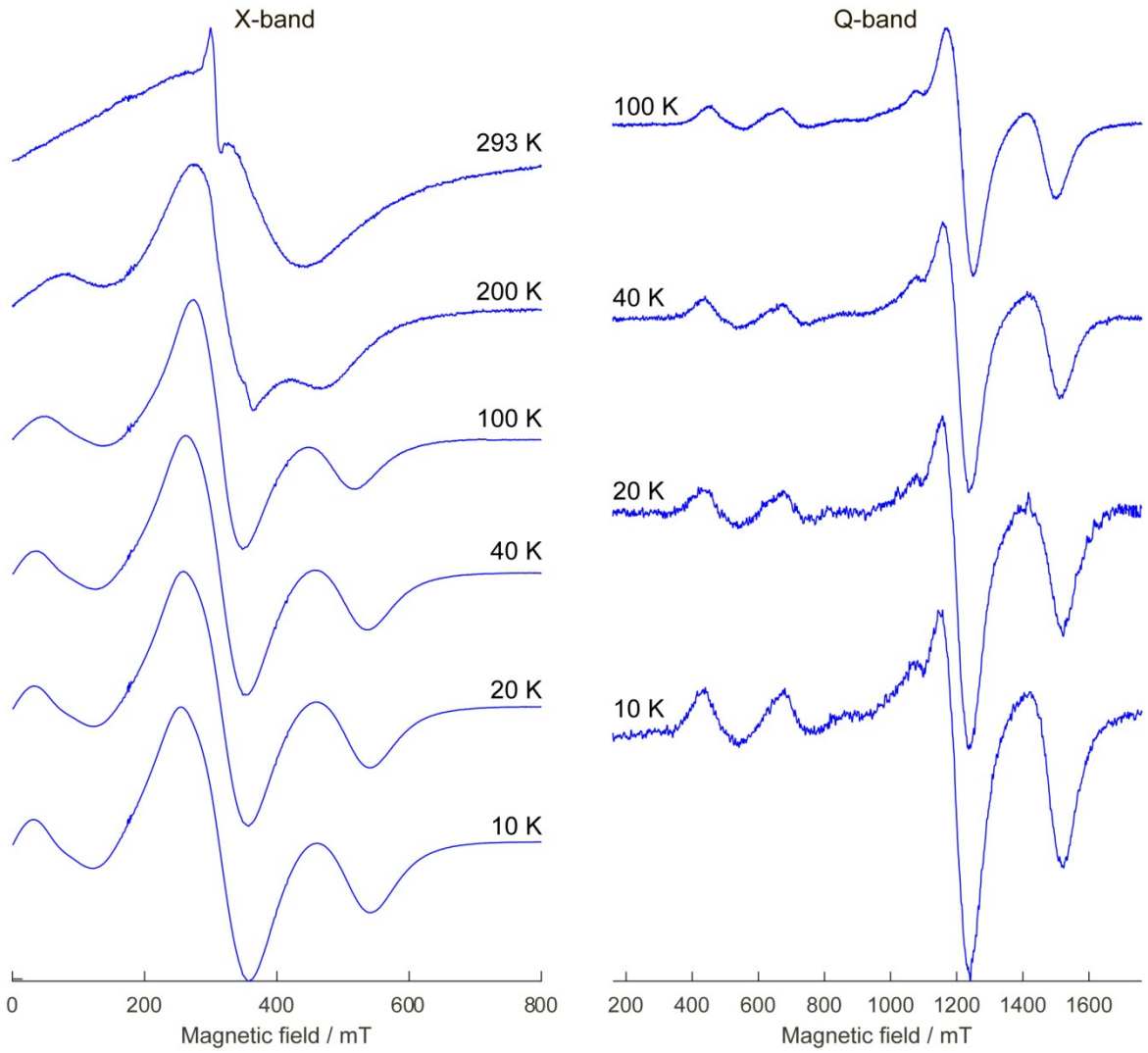


Figure S2. Temperature-dependent EPR spectra of 2 at X-band (left) and Q-band (right) (ν_{mw}≈9.75 and 33.33 GHz, respectively). All spectra are normalized, the values of temperature are indicated.

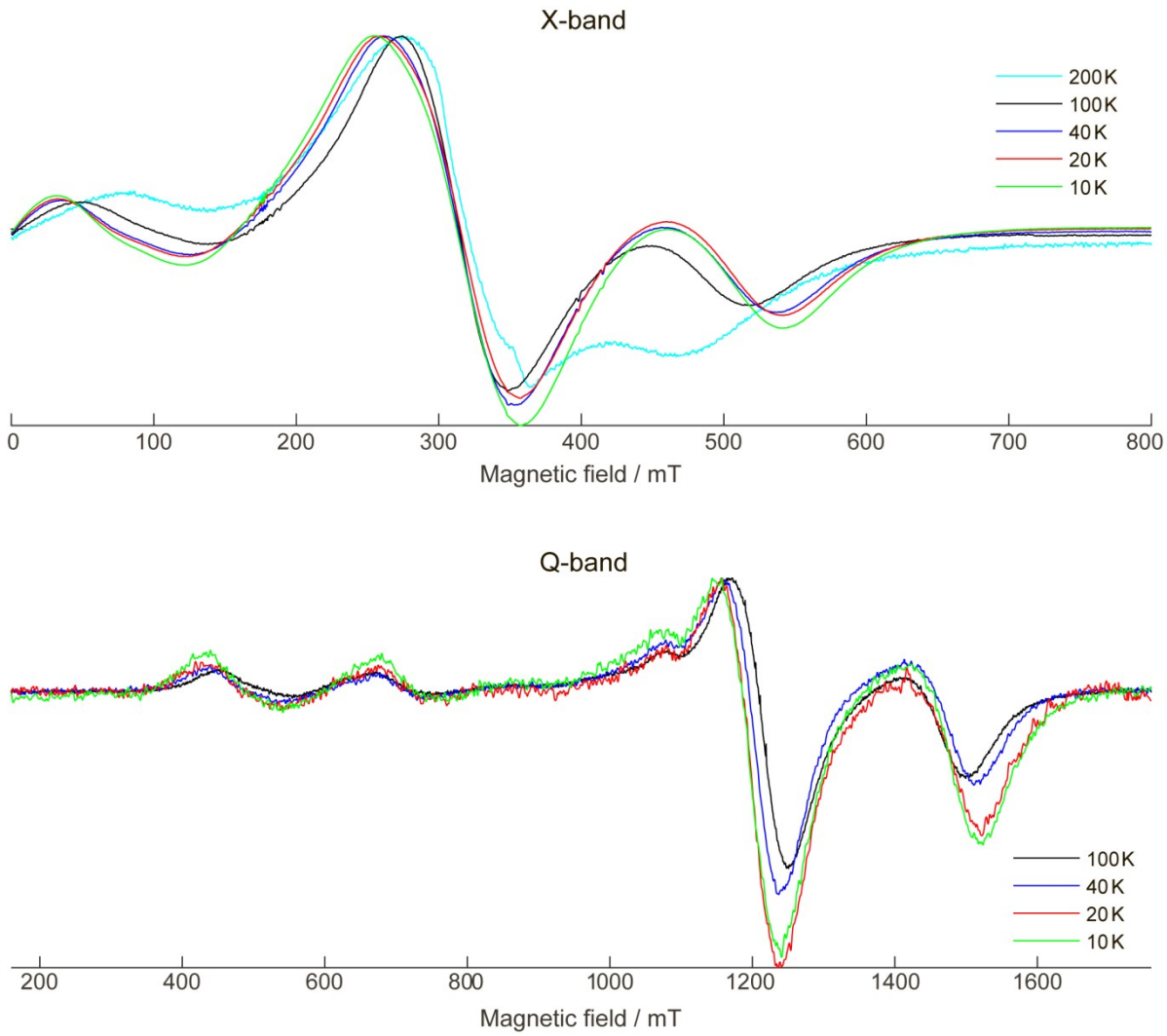


Figure S3. Temperature-dependent EPR spectra of 2 at X-band (top) and Q-band (bottom) (ν_{mw}≈9.75 and 33.33 GHz, respectively). All spectra are normalized, the values of temperature are indicated in the legend.

Table S3. Spin state (S), total energies (E_{total}), expectation values of the spin-squared operator (S^2) and exchange spin coupling parameters (J)in the electromers of the complexes **1** and **2** calculated by the DFT UB3LYP/6-311++G(d,p) method

Electromer	S	E_{total}, a.u.	S^2	$J_{SQ\text{-}SQ}$, cm^{-1}	$J_{M\text{-}SQ}$, cm^{-1}
Co(imSQ)$_2$					
Single Point					
ααα	5/2	-3049.422395	8.779	33	–665
ααβ	3/2	-3049.431923	4.588		
αβα	1/2	-3049.441752	2.390		
Optimization					
ααα	5/2	-3050.012867	8.778	40	–484
ααβ	3/2	-3050.019638	4.633		
αβα	1/2	-3050.026772	2.473		
Ni(imSQ)$_2$					
Single Point					
ααα	4/2	-3174.946725	6.026	–64	–1018
ααβ	2/2	-3174.957366	2.793		
αβα	0	-3174.967419	1.567		
Optimization					
ααα	4/2	-3175.546763	6.025	–51	–496
ααβ	2/2	-3175.551873	2.860		
αβα	0	-3175.556512	1.711		

*α corresponds to spin-up, β corresponds to spin-down; the ordering of paramagnetic centers: 1 – SQ, 2 – M, 3 – SQ

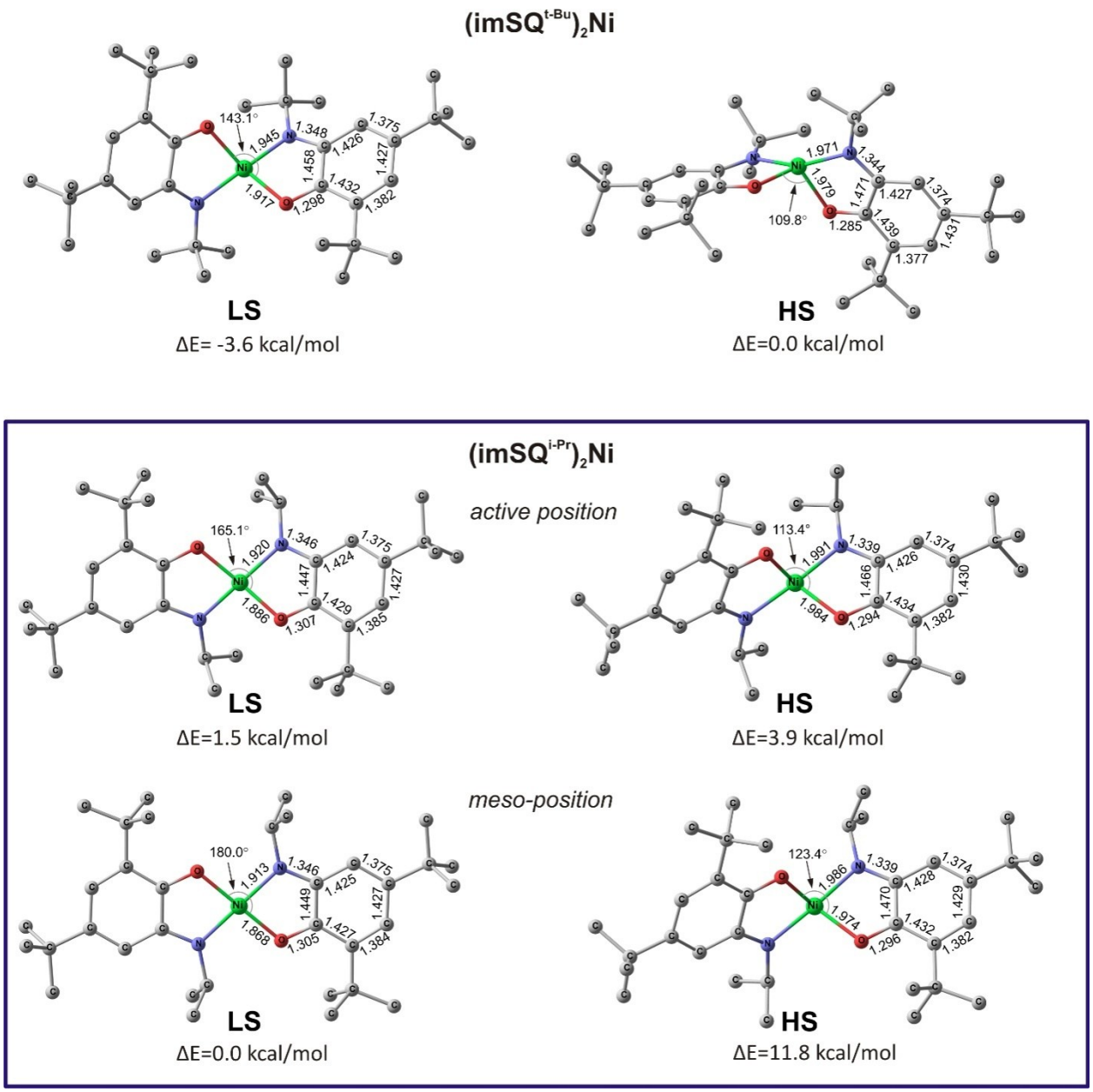
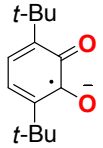
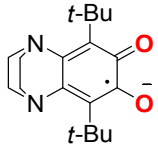
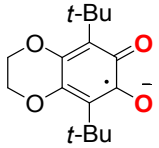
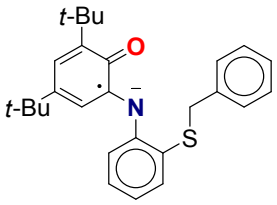
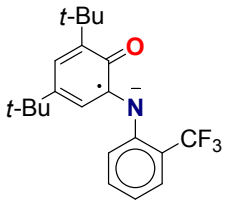
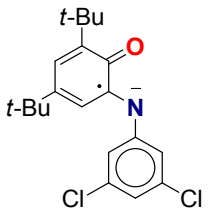
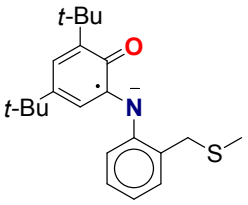
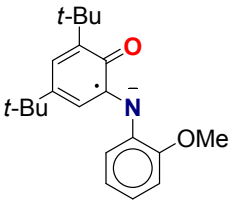
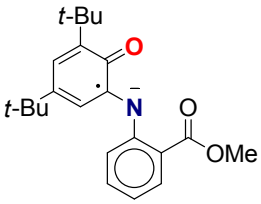
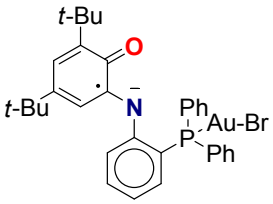
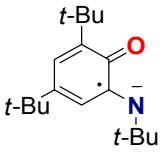
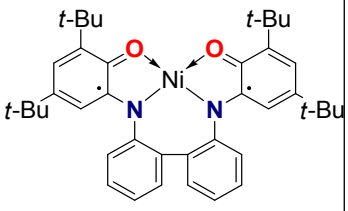
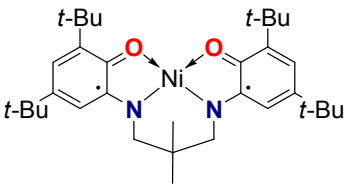
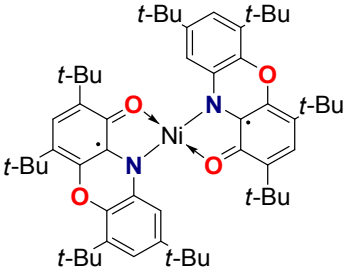
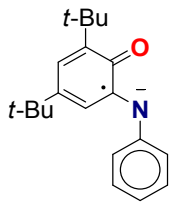
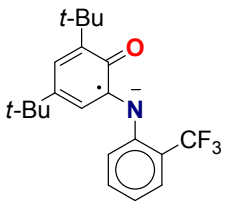
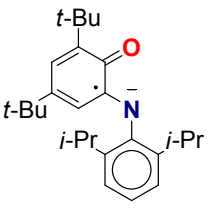
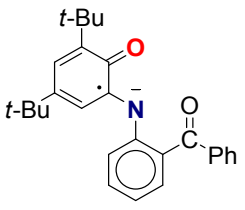
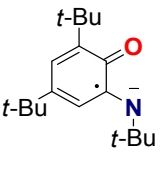


Figure S4. Optimized geometries of complex **1** and model complexes with N-*iso*-propyl substituents, calculated by the DFT UB3LYP/6-311++G(d,p) method. Hydrogen atoms are omitted for clarity. The bond lengths are given in angstroms (Å).

Table S4. The τ_4, τ_4' parameters of four coordinate nickel and cobalt bis-ligand complexes with different redox active ligands

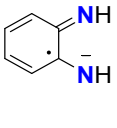
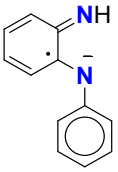
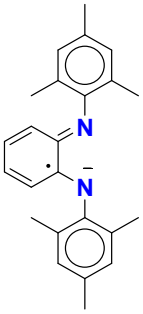
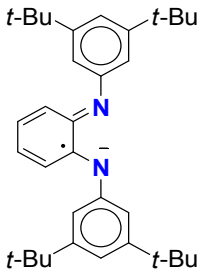
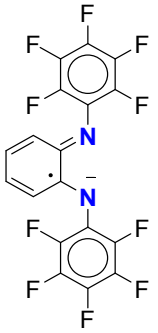
Nickel bis-*o*-benzosemiquinonates $(SQ)_2Ni$			
SQ =			
τ_4, τ_4'	0	0	0
Ref.	22	23	23

Nickel bis-*o*-iminobenzosemiquinonates $(imSQ)_2Ni$				
imSQ =				
τ_4, τ_4'	0.05; 0.04	0	0	0.04; 0.04
Ref.	26	6	24	27
imSQ =				
τ_4, τ_4'	0	0	0	0.71; 0.69
Ref.	28	28	29	This work
				
τ_4, τ_4'	0.30; 0.29	0.05; 0.05	0.64; 0.61	
Ref.	34	25	35	

	***o*-iminobenzoquinonatecobaltcomplexes $(imSQ)Co^{III}(AP)$, $imSQ_2Co^{II}$**				
imSQ =					
τ_4, τ_4'	0	0	0.04; 0.03	0	0.73; 0.70
Ref.	32	31	30	33	This work

bis-*o*-diiminobenzosemiquinonatecobaltcomplexes $(disq)_2Co^{II}$, $(disq)Co^{III}(IP)$

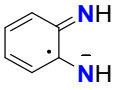
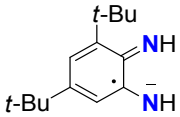
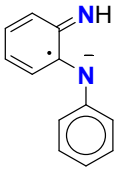
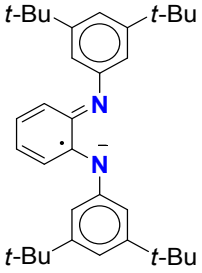
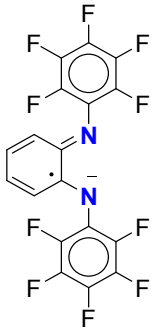
disq =

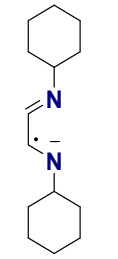
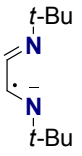
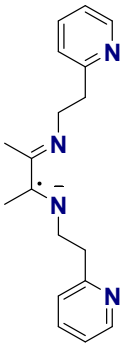
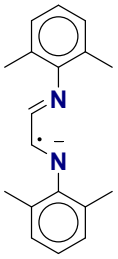
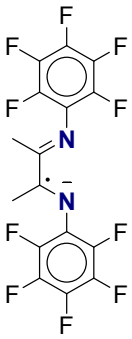
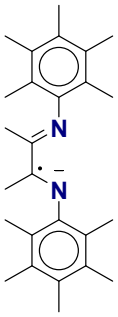
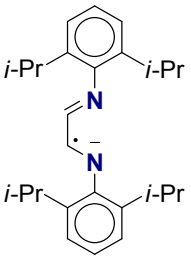
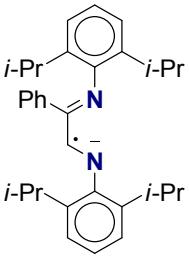
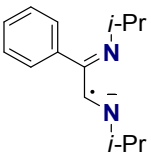
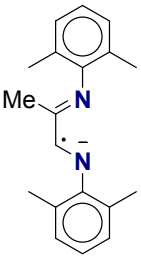
τ_4, τ_4'	0	0	0.47; 0.470	0.8; 0.8	0.48; 0.47
Ref.	1, 5	6	21	8	7

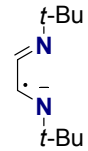
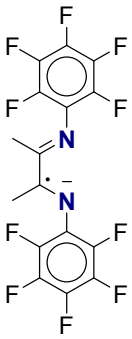
Nickel bis-*o*-diiminobenzosemiquinonates $(disq)_2Ni$

disq =

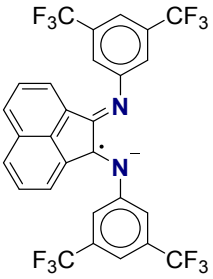
τ_4, τ_4'	0	0	0	0.85; 0.85	0.48; 0.46
Ref.	1	2	2-4	8	7

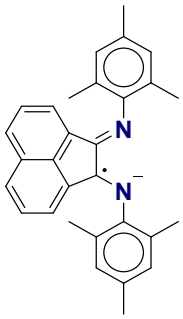
bis(1,4-diaza-1,3-butadiene)nickelcomplexes $(DAD)_2Ni$					
DAD =					
τ_4, τ_4'	0.78; 0.78	0.80; 0.79	0.67; 0.66	0.43; 0.43	0.51; 0.51
Ref.	13	10, 12	9	14	11
DAD =					
τ_4, τ_4'	0.45; 0.45	0.47; 0.47	0.78; 0.75	0.45; 0.45	0.49; 0.47
Ref.	17	18	16	15	15

bis(1,4-diaza-1,3-butadiene)cobalt complexes $(DAD)_2Co$		
DAD =		
τ_4, τ_4'	0.81; 0.81	0.53; 0.53
Ref.	10	11

bis(arylimino)acenaphthene nickel complexes $(BIAN)_2Ni$

BIAN =

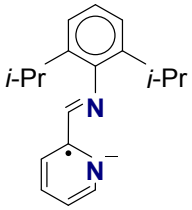




τ_4, τ_4'	0.80; 0.80	0.44; 0.44
Ref.	11	7

Bis(α-iminopyridine)metal complexes $(IP)_2M$

IP =



τ_4, τ_4'	M = Ni 0.67; 0.66	M = Co 0.71; 0.71
Ref.	20	20

References

1. A. L. Balch and R. H. Holm, *J. Am. Chem. Soc.*, 1966, **88**, 5201-5209.
2. D. Herebian, E. Bothe, F. Neese, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2003, **125**, 9116-9128.
3. H.-Y. Cheng, C.-C. Lin, B.-C. Tzeng and S.-M. Peng, *Journal of the Chinese Chemical Society*, 1994, **41**, 775-781.
4. A. A. Sidorov, P. V. Danilov, S. E. Nefedov, M. A. Golubnichaya, I. G. Fomina, O. G. Ellert, V. M. Novotortsev and I. L. Eremenko, *Russ. J. Inorg. Chem.* , 1998, **43**, 846.
5. S.-M. Peng, C.-T. Chen, D.-S. Liaw, C.-I. Chen and Y. Wang, *Inorg. Chim. Acta*, 1985, **101**, L31-L33.
6. E. Bill, E. Bothe, P. Chaudhuri, K. Chlopek, D. Herebian, S. Kokatam, K. Ray, T. Weyhermüller, F. Neese and K. Wieghardt, *Chem. Eur. J.*, 2005, **11**, 204-224.
7. M. M. Khusniyarov, K. Harms, O. Burghaus, J. Sundermeyer, B. Sarkar, W. Kaim, J. v. Slageren, C. Duboc and J. Fiedler, *Dalton Trans.*, 2008, DOI: 10.1039/b714974c, 1355-1365.
8. K. Chłopek, E. Bothe, F. Neese, T. Weyhermuller and K. Wieghardt, *Inorg. Chem.*, 2006, **45**, 6298-6307.
9. T. M. Porter, G. B. Hall, T. L. Groy and R. J. Trovitch, *Dalton Trans.*, 2013, **42**, 14689-14692.
10. T. J. Knisley, M. J. Saly, M. J. Heeg, J. L. Roberts and C. H. Winter, *Organometallics*, 2011, **30**, 5010-5017.
11. M. M. Khusniyarov, K. Harms, O. Burghaus and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2006, DOI: 10.1002/ejic.200600236, 2985-2996.
12. H. Gorls, D. Walther and J. Sieler, *Cryst. Res. Technol.*, 1987, **22**, 1145-1151.
13. M. Svoboda and H. t. Dieck, *Z. Naturforschung*, 1981, **36b**, 814-822.
14. H. t. Dieck, M. Svoboda and T. Greiser, *Z. Naturforschung*, 1981, **36b**, 823-832.
15. N. Muresan, T. Weyhermuller and K. Wieghardt, *Dalton Trans.*, 2007, DOI: 10.1039/b709390j, 4390-4398.
16. N. Muresan, K. Chlopek, T. Weyhermuller, F. Neese and K. Wieghardt, *Inorg. Chem.*, 2007, **46**, 5327-5337.
17. T. Schaub and U. Radius, *Z. Anorg. Allg. Chem.*, 2006, **632**, 807-813.
18. W. Bonrath, K. R. Pörschke, R. Mynott and C. Krüger, *Z. Naturforschung*, 1990, **45b**, 1647-1650.
19. M. J. Sgro and D. W. Stephan, *Dalton Trans.*, 2010, **39**, 5786-5794.
20. C. C. Lu, E. Bill, T. Weyhermuller, E. Bothe and K. Wieghardt, *J. Am. Chem. Soc.*, 2008, **130**, 3181-3197.
21. M. van der Meer, Y. Rechkemmer, I. Peremykin, S. Hohloch, J. v. Slageren and B. Sarkar, *Chem. Comm.*, 2014, **50**, 11104-11106.
22. G. A. Abakumov, V. K. Cherkasov, M. P. Bubnov, O. G. Ellert, Y. V. Rakitin, L. N. Zakharov, Y. T. Struchkov and Y. N. Saf'yanov, *Russ. Chem. Bull.*, 1992, 1813-1818.
23. M. P. Bubnov, N. A. Skorodumova, E. V. Baranov, A. S. Bogomyakov, V. K. Cherkasov and G. A. Abakumov, *Inorg. Chim. Acta*, 2013, **406**, 153-159.
24. P. Chaudhuri, C. N. Verani, E. Bill, E. Bothe, T. Weyhermüller and K. Wieghardt, *J. Am. Chem. Soc.*, 2001, **123**, 2213-2223.
25. K. S. Min, T. Weyhermüller, E. Bothe and K. Wieghardt, *Inorg. Chem.*, 2004, **43**, 2922-2931.
26. A. Mukherjee and R. Mukherjee, *Indian Journal of Chemistry*, 2011, **50A**, 484-490.
27. A. Paretzki, M. Bubrin, J. Fiedler, S. Zalis and W. Kaim, *Chem. Eur. J.*, 2014, **20**, 5414-5422.
28. A. V. Piskunov, I. V. Ershova, M. V. Gulenova, K. I. Pashanova, A. S. Bogomyakov, I. V. Smolyaninov, G. K. Fukin and V. K. Cherkasov, *Russ. Chem. Bull.*, 2015, **64**, 642-649.
29. D. L. J. Broere, D. K. Modder, E. Blokker, M. A. Siegler and J. I. van der Vlugt, *Angew. Chem. Int. Ed.*, 2016, **55**, 2406-2410.
30. A. I. Poddel'sky, V. K. Cherkasov, G. K. Fukin, M. P. Bubnov, L. G. Abakumova and G. A. Abakumov, *Inorg. Chim. Acta*, 2004, **357**, 3632-3640.
31. E. Bill, E. Bothe, P. Chaudhuri, K. Chlopek, D. Herebian, S. Kokatam, K. Ray, T. Weyhermuller, F. Neese and K. Wieghardt, *Chem. Eur. J.*, 2005, **11**, 204-224.
32. A. L. Smith, L. A. Clapp, K. I. Hardcastle and J. D. Soper, *Polyhedron*, 2010, **29**, 164-169.

33. A. V. Piskunov, K. I. Pashanova, A. S. Bogomyakov, I. V. Smolyaninov, A. G. Starikov and G. K. Fukin, *Dalton Trans.*, 2018, **47**, 15049-15060.
34. C. Mukherjee, T. Weyhermüller, E. Bothe and P. Chaudhuri, *Inorg. Chem.*, 2008, **47**, 11620-11632.
35. A. M. Whalen, S. Bhattacharya and C. G. Pierpont, *Inorg. Chem.*, 1994, **33**, 347-353.