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Binding of NO by nontransition metal complexes

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General specifications

All starting reagents were commercially available (Aldrich, Fluka, Strem) unless otherwise noted. Solvents were purified following standard procedures.[1] Nitric oxide was obtained by following method described in ref. 2. 3,6-Di-*tert*-butyl-*o*-benzoquinone was synthesized according to ref. 3. All manipulations on complexes were performed under conditions excluding air oxygen and moisture. X-band EPR spectra were recorded on a Bruker EMX (working frequency ~9.75 GHz) spectrometer. The g_i values were determined using DPPH as the reference (g_i = 2.0037). HFC constants were obtained by simulation with the WinEPR SimFonia Software (Bruker). UV-VIS spectra were taken with a Perkin–Elmer lambda 25 spectrometer (range 200-1100 nm), a Shimadzu UV–3600 UV/Vis/NIR spectrophotometer (range 200–2200 nm) at room temperature in the quartz cells with the thickness of 0.5 cm.

*Synthesis of (3,6-Cat)Pb (3,6-di-*tert*-butyl-catecholato)lead(II)* **1.**

Complex **1** was synthesized using method described in ref. 4.

*Synthesis of (3,6-Cat)Zn·2THF (3,6-di-*tert*-butyl-catecholato)zinc(II) ditetrahydrofuranate* **2.**

Complex **2** was synthesized using method described in ref. 5.

*The interaction of complex **1** with nitric oxide.*

The volume equivalent of NO (1 mmol, 24.5 ml) was added to the solution of complex **1** (1 mmol, 0.647 g) in 20 ml tetrahydrofuran. The color of solution changed from yellow to deep green. Complex **3** was studied by EPR and UV-VIS spectroscopy in solution. X-band EPR (THF, 293 K): g_i = 2.0015, a_i(2 ^{1}H) = 3.51 G, ai(^{207}Pb) = 63.12 G; X-band EPR (THF, 205 K): g_i = 2.0015, a_i(2 ^{1}H) = 3.51 G, a_i(^{207}Pb) = 61.10 G; a_i(^{14}N) = 0.27 G; X-band EPR (Toluene, 205 K): g_i = 2.0013, a_i(2 ^{1}H) = 3.52 G, a_i(^{207}Pb) = 79.87 G; a_i(^{14}N) = 0.38 G. UV-VIS (THF, 293 K): br. 400 nm.

*The interaction of complex **2** with nitric oxide.*

The small excess of NO (1.1 mmol) was added to the solution of complex **2** (1 mmol, 0.43 g) in 20 ml tetrahydrofuran at 0 ºC. The color of solution turned violet-blue. Complex **4** was isolated from a THF-acetonitrile solution after storage at -18 ºC overnight as a dark violet-blue powder. X-band EPR (THF, 293 K): $g_i = 2.0040$; $a_i(2\ ^1H) = 3.48$ G; $a_i(^{67}Zn) = 1.75$ G; $a_i(^{13}C) = 3.55$ G; $a_i(^{13}C) = 2.40$ G. UV-VIS (acetonitrile, 293 K): 409, 770, 845 (sh.), 990 (sh.) nm. IR (fluorinated oil, 293 K): 1715 w, 1590 w, 1492 s, 1484 s, 1467 s, 1439 m, 1392 s, 1377 s, 1353 m, 968 w, 953 w, 934 w, 915 w, 828 w, 808 m, 797 m, 677 w, 659 m, 559 w, 498 w, 436 m. IR (nujol, NaCl, 293 K): 1712 w, 1585 w, 1496 s, 1483 s, 1467 s, 1439 m, 1394 s, 1357 w, 1280m, 1234 m, 1203 w, 1148 m, 1036 w, 1025 w, 968 w, 954 w, 934 w, 916 w, 828 w, 807 m, 798 m, 675 w, 656 m.

The EPR monitoring of NO trapping.

The sample of nitrosyl complex **4** was prepared as described above. The THF solution was removed completely under vacuum and dark green powder of **4** was dried in vacuum during 2 h. Then it was dissolved in toluene and heated during 1 h. The gaseous phase was connected with evacuated ampoule containing the toluene solutions of NO-traps tris(3,6-di-*tert*-butyl-semiquinonato)cobalt(III), $(3,6\text{-SQ})_3Co$, or (1,2-bis-diphenylphosphinoethane)(3,6-di-*tert*-butyl-catecholato)nickel(II), (3,6-Cat)Ni·(dppe). Then the EPR spectrum of the corresponding cobalt or nickel nitrosyl ($(3,6\text{-SQ})Co(NO)_2$; (3,6-SQ)Ni(NO)(dppe)) was recorded.

Cobalt nitrosyl, $(3,6\text{-SQ})Co(NO)_2$: X-band EPR (toluene, 298 K): $g_i = 2.0020$, $a_i(^{59}Co) = 4.3$ G; $a_i(2\ ^1H) = 3.50$ G; $a_i(^{14}N) = 0.75$ G, data correspond to reported in ref. 6.

Nickel nitrosyl, (3,6-SQ)Ni(NO)(dppe): X-band EPR (toluene, 298 K): $g_i = 2.000$, $a_i(^{31}P) = 13.4$ G; $a_i(2\ ^1H) = 3.2$ G; $a_i(^{14}N) = 1.8$ G, data correspond to reported in ref. 7.

The diradical complexes of $(3,6\text{-SQ})_2M$ type as the products of complexes **3** and **4** disproportionation were isolated and characterized using IR and EPR spectroscopy, and these data correspond to those reported previously in refs. 4,5.

Table S1 The EPR spectral data on complexes **3** and **4**.

Complex	Solvent / T (K)	g_{iso}	$a_i(^1H)$ (G)	$a_i(E)$ (G)
3	THF / 293	2.0015	2 ^{1}H 3.51	^{207}Pb 63.12
3	THF / 205	2.0015	2 ^{1}H 3.51	^{207}Pb 61.10 ^{14}N 0.27
3	Toluene / 205	2.0013	2 ^{1}H 3.52	^{207}Pb 79.87 ^{14}N 0.38
4	THF / 293	2.0040	2 ^{1}H 3.48	^{67}Zn 1.75 ^{13}C 3.55 ^{13}C 2.40

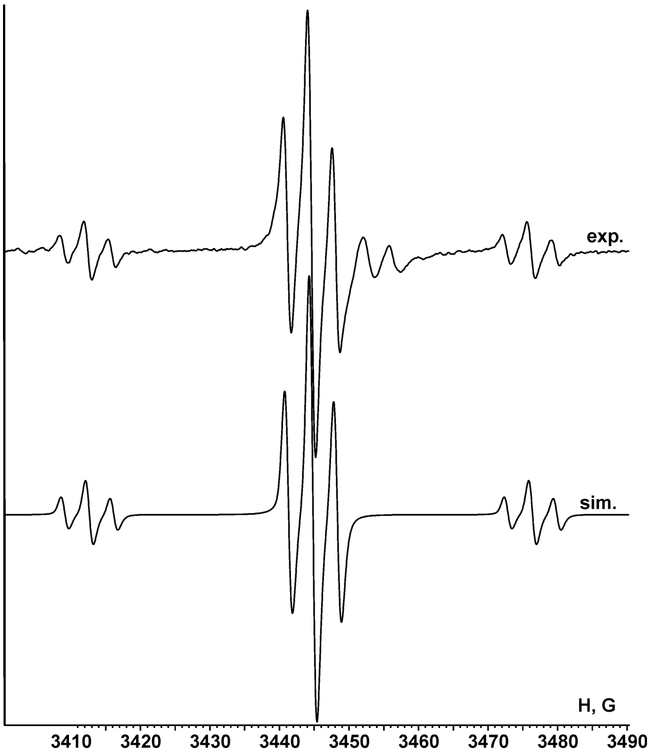

Figure S1 Experimental X-band EPR spectrum of **3** (THF, 293 K) (exp.) and its computer simulation (sim.) (WinEPR SimFonia 1.25).

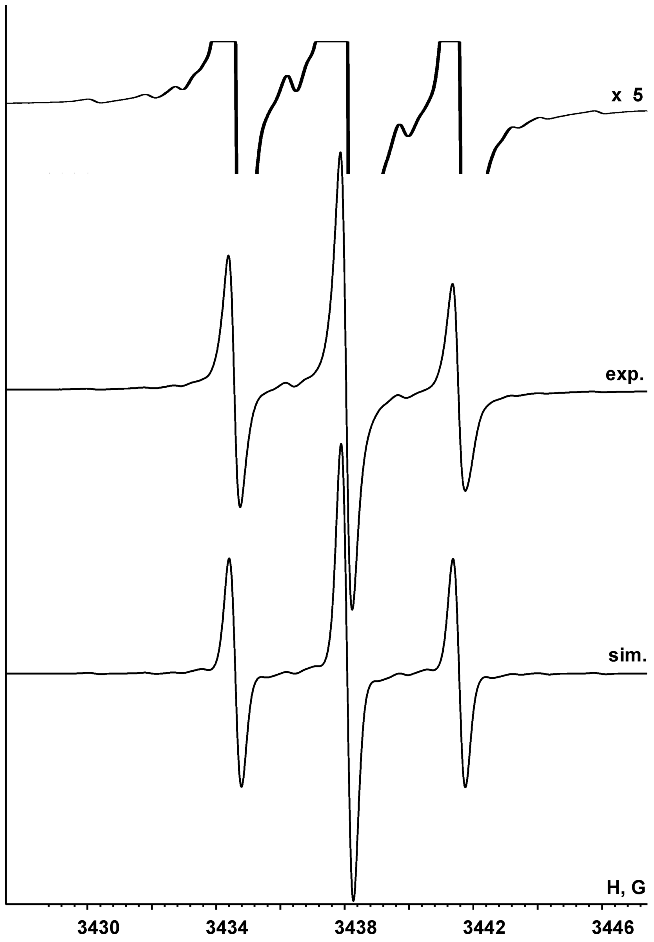

Figure S2 Experimental (THF, 293K) X-band EPR spectrum of **4** (exp.) and its computer simulation (sim.) (WinEPR SimFonia 1.25).

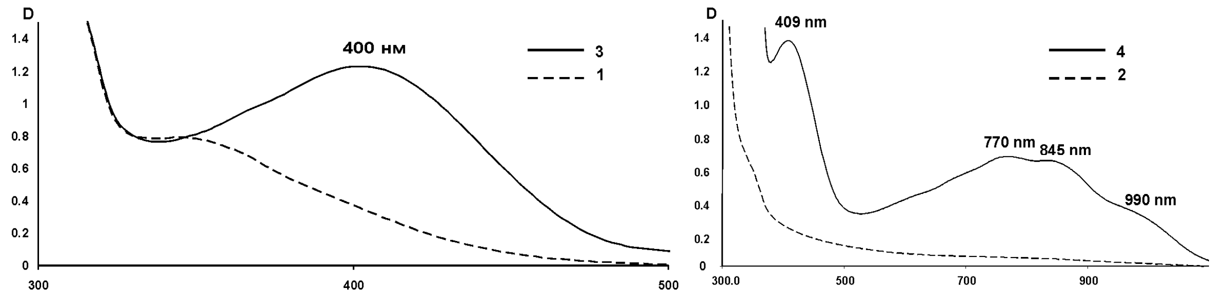

Figure S3 UV-VIS spectra of initial lead(II) and zinc(II) catecholates and generated nitrosyl-containing products [THF, RT (**1**, **3**) and acetonitrile, RT (**2**, **4**)].

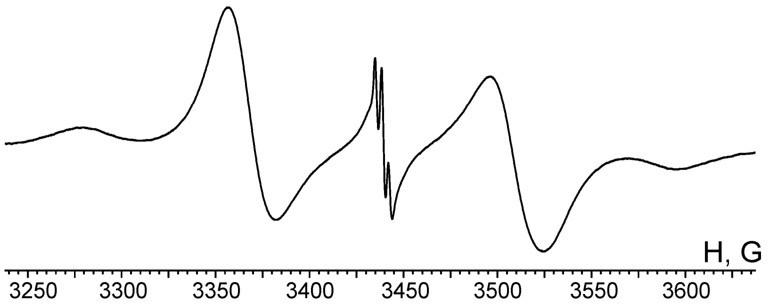

Figure S4 Experimental (frozen THF, 150K) X-band EPR spectrum of $(3,6\text{-SQ})_2Zn$ (exp.) as the product of the disproportionation of zinc complex **4**.

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