Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Mendeleev Commun., 2012, **22**, 208–210
Mendeleev Communications

Binding of NO by nontransition metal complexes

Ekaterina V. Ilyakina, Andrey I. Poddel'sky,* Vladimir K. Cherkasov and Gleb A. Abakumov

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, 603950 Nizhnii Novgorod, Russian Federation. Fax: +7 831 462 7497; e-mail: aip@iomc.ras.ru

DOI: 10.1016/j.mencom.2012.06.013

The first example of nitric oxide fixation by nontransition metal complexes was found: lead(II) and zinc(II) catecholato complexes readily react with nitric oxide to give the corresponding nitrosyl-containing mono-*o*-semiquinonates; the process of binding and transfer of NO can be easily monitored by EPR spectroscopy.

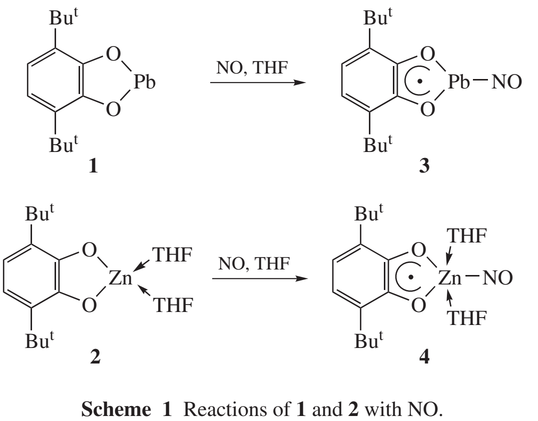
The importance of chemical and biochemical processes with nitrogen(II) oxide[1–3] has stimulated the studies of NO reactivity towards transition metal complexes and organic substrates.[4–6] However, the reactivity of nontransition metal complexes in relation to nitrogen(II) oxide has not been reported.

The metal complexes containing redox-active *o*-quinone and related ligands are the promising objects in terms of fundamental and applied sciences.[7] These compounds reveal exceptional properties caused by the ability of redox-active ligands to reversible oxidation and reduction in a metal coordination sphere.[7,8] The combination of redox-active ligand and nontransition metal in a molecule allows one to model chemical behaviour of transition metal complexes.[9–11] For example, antimony(V) *o*-amidophenolates and catecholates were found to bind and release molecular oxygen under mild conditions,[9] gallium complex of chelating diamide ligand is able to add reversibly alkynes.[10] In general, such reactivity is due to the redox activity of ligand rather than metal.

Here, we describe the spectroscopic studies of the reactions of lead(II) and zinc(II) catecholates with nitrogen(II) oxide yielding the corresponding nitrosyl complexes.

Nontransition metal catecholato complexes are successfully used as spin traps for various paramagnetic species,[12] however, interactions of these complexes (and in general, nontransition metal complexes) with nitric oxide (NO), which is a radical species in the ground state, are unfairly less studied although analogous interactions are well known in the case of transition metal complexes.[4,5] We have found that Pb^{II} and Zn^{II} catecholates **1** and **2** react easily with NO in THF solutions to produce paramagnetic species **3** and **4**, respectively (Scheme 1).

The EPR spectral data on complexes **3** and **4** are collected in Table S1 of Online Supplementary Materials. The observed EPR spectra of complexes **3** and **4** are typical of mono-*o*-semiquinonato species of these metals.[13] Thus, upon the addition of NO, the catecholato ligand undergoes one-electron oxidation to the corresponding *o*-semiquinonato species, while NO receives one electron and forms an anionic nitrosyl ligand (Scheme 1).



Scheme 1 Reactions of **1** and **2** with NO.

The hyperfine structure in the EPR spectra of **3**, **4** is caused by the hyperfine coupling (HFC) of unpaired electron with two aromatic protons in the 4- and 5-positions of *o*-semiquinonato ligand and satellite splitting on magnetic lead (^{207}Pb, $I = 1/2$, 22.1%[14]) for **3** (Figure S1) or zinc isotopes (^{67}Zn, $I = 5/2$, 4.1%) for **4** (Figure S2). The relatively wide line in the EPR spectrum of lead complex **3** ($\Delta H \approx 1$ G) at room temperature even at low concentration of complex suggests supplemental splitting with

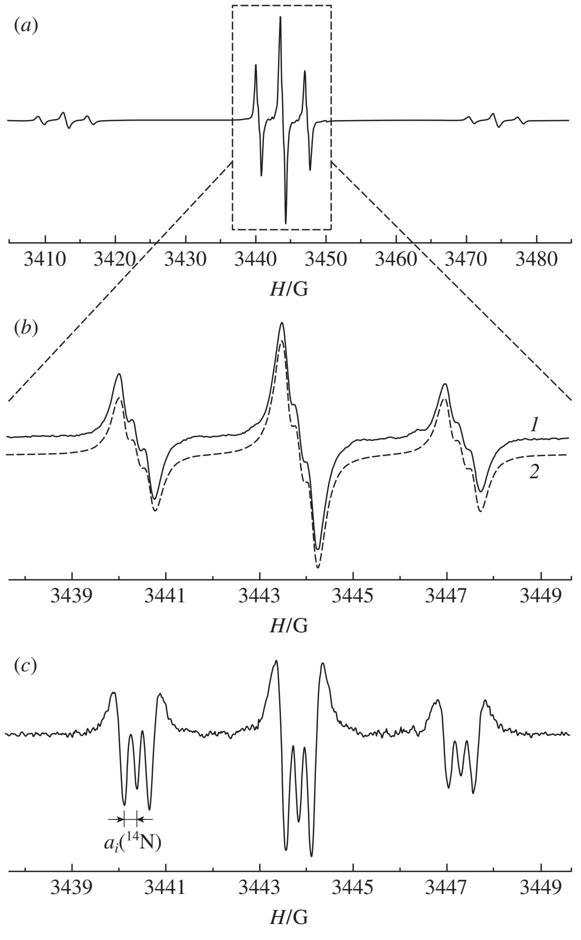
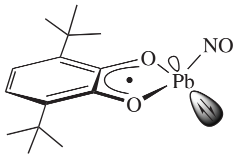


Figure 1 (*a*) Experimental X-band EPR spectrum of **3** (THF, 205 K); (*b*) the main component of (*1*) experimental spectrum and (*2*) its computer simulation (WinEPR SimFonia 1.25); (*c*) the 2nd derivative of the main component of EPR signal.

a small HFC constant. Lowering the temperature allows us to resolve the EPR spectrum of **3**: one can observe hyperfine structure on nitrogen isotope of NO ligand (^{14}N, $I = 1$, 99.636%[14]) with a value of 0.27 G (Figure 1, Table S1).

It is well known that HFC constants with magnetic nuclei (phosphorus, nitrogen, halogens, *etc*.) of additional ligands in *o*-semiquinonato complexes are sensitive to the coordination geometry and the relative position of semiquinonato and additional ligands: HFC constant on nucleus for ligand in an apical position is usually one order of magnitude higher than the HFC constant for ligand in a plane of SQ radical-anion.[15] Moreover, in the latter case, HFC may not be occasionally observed. The observation of HFC on the nitrogen atom of NO ligand can be explained on the basis of a distorted trigonal pyramidal structure of generated complex **3** (Scheme 2).[13(*b*),(*c*),15] In this case, HFC with the ^{14}N isotope is observed due to the interaction of MO of nitrosyl ligand with π-MO of *o*-semiquinonato ligand containing an unpaired electron.

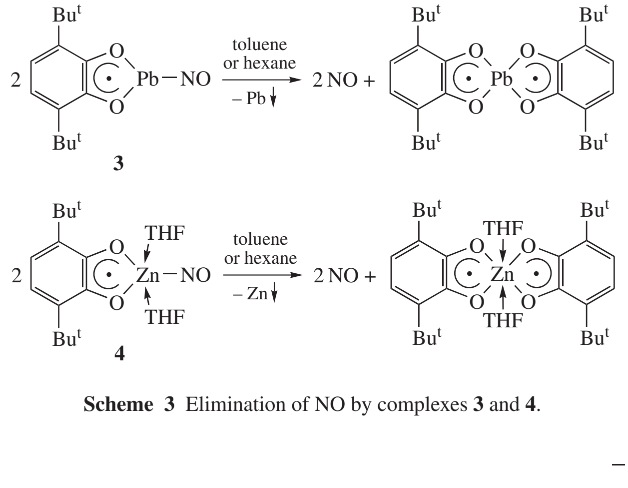


Scheme 2 Distorted trigonal pyramidal structure of **3**.

A different situation takes place in the case of zinc complex **4**. The EPR line width is low and the EPR spectrum of **4** does not contain HFC on the nitrogen atom of NO ligand as the consequence of trigonal bipyramidal geometry, where NO$^-$ lies in the plane of paramagnetic SQ ligand and makes a low contribution in π-MO of unpaired electron.

The interaction of complexes **1**, **2** with NO proceeds with a colour change from pale yellow to deep green for lead complex **1** and from nearly colourless to deep blue-violet for zinc complex **2**. The UV-VIS spectra of complexes **1**–**4** are shown in Figure S3. In both cases, the addition of NO leads to the appearance of intense absorptions at 400, 409 nm typical of complexes with anion-radical *o*-semiquinonato ligand. Complex **4** can be isolated from a THF–acetonitrile mixture at a low temperature (–30 °C) as dark blue-violet powder, which demonstrates the band at 1392 cm^{-1} which can be attributed to stretching vibrations of the coordinated NO$^-$ group. This band is absent in initial catecholato zinc(II) complex **2** or in zinc(II) bis-*o*-semiquinolate as a product of disproportionation of complex **4** (see below). Solid product **4** cannot be stored for a long time even under air- and water-free conditions.

Complexes **3**, **4** are stable in THF solution, while the change of THF with toluene or hexane results in the disproportionation of **3**, **4** to the corresponding diradical bis-*o*-semiquinonato species of (3,6-SQ)$_2$M type and elimination of NO (Scheme 3).



Scheme 3 Elimination of NO by complexes **3** and **4**.

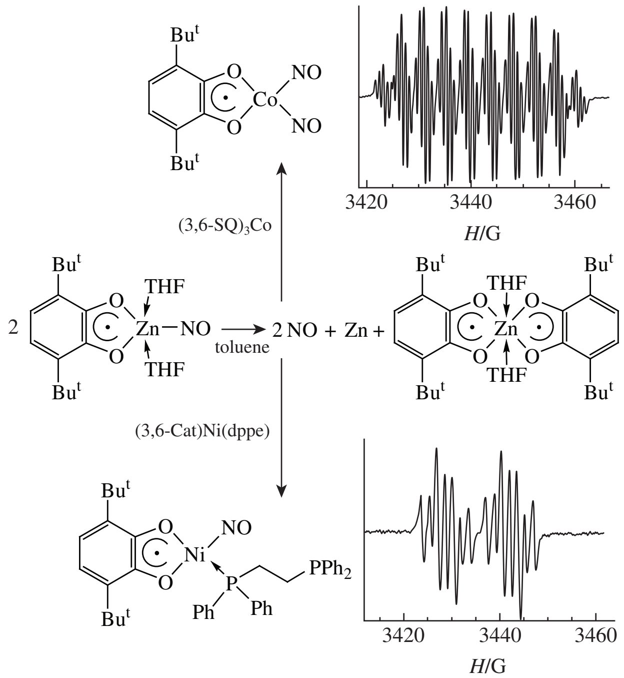


Figure 2 Monitoring of NO elimination by (3,6-SQ)Zn(NO)·2THF **4** in toluene solution.

In this case, the disappearance of signals from **3**, **4** in EPR spectra is accompanied by the appearance of broad signals of diradical species (Figure S4).

The disproportionation of **3**, **4** in nonpolar solvents and the elimination of NO was monitored by EPR using NO traps on the basis of transition metal *o*-quinonato complexes. Tris(3,6-di-*tert*-butylsemiquinonato)cobalt(III), (3,6-SQ)$_3$Co, and (1,2-bis-diphenylphosphinoethane)(3,6-di-*tert*-butylcatecholato)nickel(II), (3,6-Cat)Ni·(dppe) react easily with gaseous NO with the formation of the stable paramagnetic nitrosyl derivatives (3,6-SQ)Co(NO)$_2$[16] and (3,6-SQ)Ni(NO)(dppe),[17] respectively, possessing characteristic EPR spectra. These complexes were applied as traps of NO eliminated after dissolving and storage of **3**, **4** in toluene. Nitric oxide elimination by complex **4** and fixation processes are well illustrated in Figure 2. The formation of cobalt and nickel nitrosyls verifies the elimination of NO by complexes **3** and **4** in nonpolar solvents.

In summary, the 3,6-di-*tert*-butylcatecholato complexes of lead(II) and zinc(II) demonstrate the first example of nitrogen(II) oxide fixation by nontransition metal complexes. Such unique reactivity typical of transition metal complexes is achieved due to the presence of a redox-active ligand. The presence of a paramagnetic radical-anion in the coordination sphere of generated complexes makes it possible to effectively monitor NO addition using EPR spectroscopy.

This work was supported by the Russian Foundation for Basic Research (grant no. 10-03-00788), the President of the Russian Federation (grant nos. NSh-1113.2012.3 and MK-614.2011.3) and the Russian Science Support Foundation (E.V.I.) This work was performed according to FSP 'Scientific and Scientific-Pedagogical Cadres of Innovation Russia' for 2009–2013 (state contract P982 from 27.05.2010).

Online Supplementary Materials

Supplementary data (experimental procedures, experiments on NO binding, Table S1, Figures S1–S4 containing EPR and UV-VIS data) associated with this article can be found in the online version at doi:10.1016/j.mencom.2012.06.013.

References

1 (*a*) R. J. P. Williams, *Chem. Soc. Rev.*, 1996, **25**, 77; (*b*) G. B. Richter-Addo, P. Legzdins and J. Burstyn, *Chem. Rev.*, 2002, **102**, 857.

2 (*a*) R. Shimanovich and J. T. Groves, *Arch. Biochem. Biophys.*, 2001, **387**, 307; (*b*) R. Shimanovich, S. Hannah, V. Lynch, N. Gerasimchuk, T. D. Mody, D. Magda, J. Sessler and J. T. Groves, *J. Am. Chem. Soc.*, 2001, **123**, 3613.

3 (*a*) B. E. Mann and R. Motterlini, *Chem. Commun.*, 2007, 4197; (*b*) C. Napoli and L. J. Ignarro, *Annu. Rev. Pharmacol. Toxicol.*, 2003, **43**, 97.

4 (*a*) J. A. Olabe and L. D. Slep, in *Comprehensive Coordination Chemistry II*, eds. J. A. McCleverty, T. J. Meyer and A. B. P. Lever, Elsevier–Pergamon, Amsterdam, New York, Oxford, 2003, vol. 1, p. 603; (*b*) G. B. Richter-Addo and P. Legzdins, *Metal Nitrosyls*, Oxford University Press, New York, 1992.

5 (*a*) T. W. Hayton, P. Legzdins and W. B. Sharp, *Chem. Rev.*, 2002, **102**, 935; (*b*) M. Wolak and R. van Eldik, *Coord. Chem. Rev.*, 2002, **230**, 263; (*c*) M. Hoshino, L. Laverman and P. Ford, *Coord. Chem. Rev.*, 1999, **187**, 75.

6 J. Hartung, *Chem. Rev.*, 2009, **109**, 4500.

7 (*a*) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **219–221**, 415; (*b*) A. I. Poddel'sky, V. K. Cherkasov and G. A. Abakumov, *Coord. Chem. Rev.*, 2009, **253**, 291.

8 (*a*) A. Caneschi and A. Dei, *Angew. Chem. Int. Ed.*, 1998, **37**, 3005; (*b*) C. G. Pierpont, *Coord. Chem. Rev.*, 2001, **216–217**, 99; (*c*) G. A. Abakumov, G. A. Razuvaev, V. I. Nevodchikov and V. K. Cherkasov, *J. Organomet. Chem.*, 1988, **341**, 485.

9 (*a*) V. K. Cherkasov, G.A. Abakumov, E. V. Grunova, A. I. Poddel'sky, G. K. Fukin, E. V. Baranov, Yu. A. Kurskii and L. G. Abakumova, *Chem. Eur. J.*, 2006, **12**, 3916; (*b*) A. I. Poddel'sky, I. V. Smolyaninov, Yu. A. Kurskii, G. K. Fukin, N. T. Berberova, V. K. Cherkasov and G. A. Abakumov, *J. Organomet. Chem.*, 2010, **695**, 1215.

10 I. L. Fedushkin, A. S. Nikipelov and K. A. Lyssenko, *J. Am. Chem. Soc.*, 2010, **132**, 7874.

11 G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, O. Yu. Trofimova and G. V. Romanenko, *Dokl. Akad. Nauk*, 2010, **434**, 344 [*Dokl. Chem.* (*Engl. Transl.*), 2010, **434**, 237].

12 (*a*) A. V. Lado, A. V. Piskunov, V. K. Cherkasov, G. K. Fukin and G. A. Abakumov, *Koord. Khim.*, 2006, **32**, 181 (*Russ. J. Coord. Chem.*, 2006, **32**, 173); (*b*) A. V. Piskunov, A. V. Lado, E. V. Ilyakina, G. K. Fukin, E. V. Baranov, V. K. Cherkasov and G. A. Abakumov, *J. Organomet. Chem.*, 2008, **693**, 128.

13 (*a*) R. R. Rakhimov, P. M. Solozhenkin, V. S. Pupkov and A. I. Prokof'ev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 699 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 619); (*b*) G. A. Abakumov, V. K. Cherkasov, A. V. Piskunov, A. V. Lado, G. K. Fukin and L. G. Abakumova, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 1103 (*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 1146); (*c*) G. M. Barnard, M. A. Brown, H. E. Mabrouk, B. R. McGarvey and D. G. Tuck, *Inorg. Chim. Acta*, 2003, **349**, 142.

14 *Handbook of Chemistry and Physics*, 84th edn., ed. D. R. Lide, CRC Press, 2003–2004.

15 (*a*) A. G. Davies and J. A.-A. Hawari, *J. Organomet. Chem.*, 1983, **251**, 53; (*b*) A. I. Prokof'ev, S. I. Pombrik, Z. K. Kasymbekova, N. N. Bubnov, S. P. Solodovnikov, D. N. Kravtsov and M. I. Kabachnik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 540 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1982, **31**, 482); (*c*) G. A. Razuvaev, V. K. Cherkasov and G. A. Abakumov, *J. Organomet. Chem.*, 1978, **160**, 361; (*d*) K. A. Kozhanov, M. P. Bubnov, V. K. Cherkasov, G. K. Fukin and G. A. Abakumov, *Chem. Commun.*, 2003, 2610; (*e*) G. A. Abakumov, I. A. Teplova, V. K. Cherkasov and K. G. Shalnova, *Inorg. Chim. Acta*, 1979, **32**, L57; (*f*) A. Y. Girgis, Y. S. Sohn and A. L. Balch, *Inorg. Chem.*, 1975, **14**, 2327; (*g*) E. V. Ilyakina, A. I. Poddel'sky, A. V. Piskunov and N. V. Somov, *Inorg. Chim. Acta*, 2012, **380**, 57.

16 L. G. Abakumova, K. G. Shal'nova, A. V. Lobanov, G. A. Abakumov and V. K. Cherkasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 674 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 574).

17 G. A. Abakumov, V. K. Cherkasov, V. I. Nevodchikov, I. A. Teplova, L. G. Abakumova and M. P. Bubnov, *Dokl. Akad. Nauk*, 1995, **341**, 767 (in Russian).

Received: 6th February 2012; Com. 12/3874