CHEMISTRY AND APPLICATIONS OF CYANOXIMES AND THEIR METAL COMPLEXES

by

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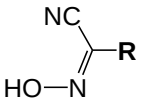
During the last three decades research interests were dedicated to the new subclass of organic ligands – cyanoximes – that have general formula NC-C(=NOH)-R where R is an electron-withdrawing group. Presence of CN-group makes cyanoximes ~10,000 more acidic and better ligands than other known oximes. With 38 different R groups the most abundant is the family of *mono*-cyanoximes **1** (below), followed by *bis*-cyanoximes **2**-**4** that include aromatic and aliphatic spacers, and lately *tris*-cyanoxime **5** - a tripod - was obtained and characterized.



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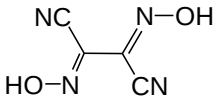

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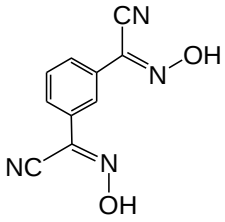

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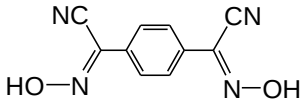

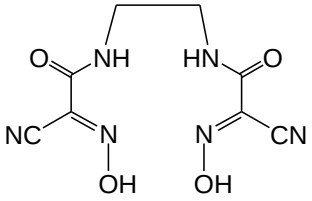

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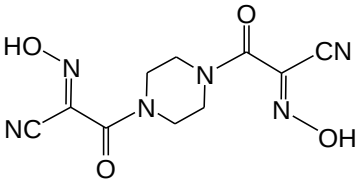

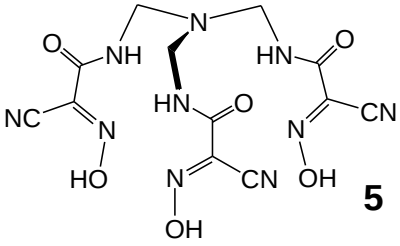

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These simple low molecular weight organic molecules represent series of new excellent ampolydentate ligands for coordination chemistry: new types of *molecular Legos*. Both un-complexed ligands, their Na^+ and K^+ salts and other metal complexes show a large spectrum of biological activity from growth regulation in plants to significant *in vitro* and *in vivo* cytotoxicity against human cancers. Currently 44 cyanoximes are known, and there were more than two hundreds cyanoxime complexes synthesized and studied using a variety of different spectroscopic methods and X-ray analysis. Methods of syntheses, stereochemistry of cyanoximes ligands, their structures and properties, as well as the most interesting coordination compounds are reviewed in this presentation. A broad spectrum of practical applications of both cyanoximes, and their metal complexes is outlined in this lecture as well.

Some of the most representative citations:

[1] N.Gerasimchuk, K. Bowman-James. *Encyclopedia of Inorganic Chemistry*, v.5, John Wiley & Sons, **1994**, 2254-2269.
[2] A.A. Mokhir, K.V. Domasevich, et al., *Inorganica Chimica Acta*, **1999**, *284*, 85-98.
[3] K.V. Domasevitch, N. Gerasimchuk, et al., *Inorganic Chemistry*, **2000**, *39* (6), 1227.
[4] D.Eddings, C.Barnes, N.Gerasimchuk, et al. *Inorganic Chemistry*, **2004**, *43* (13), 3894.
[5] D. Robertson, J. F. Cannon, N. Gerasimchuk. *Inorganic Chemistry*, **2005**, *44* (23), 8326.
[6] Maher, T.; Gerasimchuk, N.; Durham, P.; Domasevitch, K.V.; Wilking, J.; Mokhir, A. *Inorganic Chemistry*, **2007**, *46* (18), 7268.
[7] Owen, T.; Grandjean, F.; Long, G.J.; Domasevitch, K.V.; Gerasimchuk, N. *Inorganic Chemistry*, **2008**, *47* (19), 8704.
[8] Ilkun, O.T.; Archibald, S.; Barnes, C.L.; Gerasimchuk, N.; Biagioni, R.; Silchenko, S.; Gerasimchuk, O.A.; Nemykin, V. *Dalton Transactions*, **2008**, 5715.
[9] Glower G.; Gerasimchuk, N.; Biagioni, R.; Domasevitch, K..V. *Inorganic Chemistry*. **2009**, *48* (6), 2371.
[10] Gerasimchuk, N.; Esaulenko, A.N.; Dalley, K.N.; Moore, C. *Dalton Transactions*, **2010**, *39*, 749-764.
[11] Gerasimchuk, N.; Gamian, A.; Glover, G.; Szponar, B. *Inorganic Chemistry.* **2010**, *49* (21), 9863-9874.
[12] Gerasimchuk, N. *Polymers* **2011**, *3*, 2-37
[13] D. Marcano, N. Gerasimchuk, V. Nemykin, and S. Silchenko. *Cryst. Growth & Des*., **2012**, *12*, 2877-2889.
[14] Ratcliff, J.; Kuduk-Jaworska, J.; Chojnacki, H.; Nemykin, V.N.; Gerasimchuk, N. *Inorganica Chimica Acta.* **2012**, *385*, 1-11.
[15] Ratcliff, J.; Durham, P.; Keck, M.; Mokhir, A.; Gerasimchuk, N. *Inorganica Chimica Acta*. **2012**, *385*, 11-20.
[16] Cheadle, C.; Gerasimchuk, N.; Barnes, C.L.; Tyukhtenko, S.I.; Silchenko, S. *Dalton Transactions*. **2013**, *42* (14), 4931 – 4946.
[17] Gerasimchuk, N. *Eur. J. Inorg. Chem*. **2014**, 4518–4531.
[18] Marcano, D.C.; Lindeman, S.V.; Pyrkosz-Bulska, M.; Gumienna-Kontecka, E.; Lengyel, A.; Kuzmann, E.; Röminger, F.; Gerasimchuk, N. *Current Inorganic Chemistry*, **2015**, *5* (2), 98-113.
[19] Gerasimchuk, N.; Guzei, I.; Sipos, P. *Current Inorganic Chemistry*, **2015**, *5* (1), 38-63.
[20] Klaus, D.R., Keene, M., Silchenko, S., Berezin, M., Gerasimchuk, N. *Inorganic Chemistry*, **2015**, *54* (4), 1890-1900.
[21] Mann, A.; Gerasimchuk, N.; Silchenko, S. *Inorganica Chimica Acta*, **2016**, *440*, 118–128.
[22] Adedamola A. Opalade, Karmakar, A.; G. M. D. M. Rúbio, Pombeiro, A.J.L; Gerasimchuk, N. *Inorganic Chemistry*, **2017**, *56* (22), 13962–13974.
[23] Cheadle, C.; Ratcliff, J.; Berezin, M.; Pal'shin, V.; Nemykin, V.N.; Gerasimchuk, N. *Dalton Transactions*, **2017**, *46*, 13562-1382.
[24] Gerasimchuk, N. *Dalton Transactions*, **2019**, *48*, 7985–8013.