

CHEM 304: π -Acceptor Ligands

Topic: Examples of metal nitrosyls with structural data

Table. The literature data on the bond lengths, bond angles, and infrared spectroscopic $\nu(\text{NO})$ vibrations of different metal nitrosyl complexes; x denotes the number of $\{\text{Fe}(\text{NO})_n\}^x$ valence electrons according to the Enemark and Feltham notation. Along, the reference documents are given in the last column.

Complex	x	$\nu(\text{NO})$ (cm^{-1})	$\angle \text{MNO}$ ($^\circ$)	$d\text{M}-\text{N}$ (\AA)	$d\text{N}-\text{O}$ (\AA)	Reference
$[\text{Ru}(\text{pybuS}_4')(\text{HNO})]$	8	1358	130	1.875	1.242	[1]
$[\text{OsCl}_2(\text{CO})(\text{PPh}_3)_2(\text{HNO})]$	8	1410	136.9	1.915	1.193	[2]
$[\text{IrHCl}_2(\text{PPh}_3)_2(\text{HNO})]$	8	1493	129.8	1.879	1.235	[3]
$[\text{Co}(\text{NO})(\text{diars})_2(\text{NCS})]^+$	8	1587	132			
$[\text{Fe}(\text{PaPy}_3)\text{NO}](\text{ClO}_4)$	7	1615	141.29	1.7515	1.19	[4]
$[\text{Fe}(\text{cyclam-ac})\text{NO}](\text{PF}_6)$	7	1615	148.7	1.722	1.166	[5]
$[\text{Fe}(\text{NO})(\text{diars})_2(\text{NCS})]^+$	7	1620	159			
$[\text{Fe}(\text{NO})(\text{pyN}_4)]^{2+}$	7	1620	139			
$[\text{Fe}(\text{pyN}_4)\text{NO}]\text{Br}_2$	7	1620	139.4	1.737	1.175	[6]
$[\text{Fe}(\text{TPP})(\text{I-Melm})\text{NO}]$	7	1625	142.1	1.743	1.121	[7]
$[\text{Co}(\text{NO})(\text{S}_2\text{CNMe}_2)_2]$	8	1630	136			
$[\text{Fe}('pyS}_4')\text{NO}]$	7	1648	143.8	1.712	1.211	[8]
$[\text{Fe}(\text{NO})(\text{oep})]$	7	1666	144			
$[\text{Fe}(\text{T pivPP})(\text{NO}_2)\text{NO}]$	7	1668	137.4	1.84	1.134	[9]
$[\text{Fe}(\text{NO})(\text{tpp})]$	7	1670	149			
$[\text{Co}(\text{NO})(\text{oep})]$	8	1677	123			[10]
$[\text{Fe}(\text{Lpr})\text{NO}]$	7	1682	147	1.749	1.182	[11]
$[\text{Fe}(\text{NO})(\text{S}_2\text{CNMe}_2)_2]$	7	1690	170			
$[\text{Fe}(\text{Me}_3\text{TACN})(\text{N}_3)_2\text{NO}]$	7	1690	155.5	1.738	1.142	[12]
$[\text{Fe}(\text{NO})(\text{salen})]$	7	1710	147			
$[\text{Fe}(\text{NO})(\text{diars})_2]^{2+}$	7	1760	173			
$(\text{PPh}_4)_2[\text{OsCl}_5\text{NO}]$	6	1802	178.5	1.83	1.147	[13]
$[\text{Fe}(\text{NO})(\text{oep})]^+$	6	1838	173			
$[\text{Fe}(\text{NO})(\text{oep})(\text{C}_6\text{H}_4\text{F-p})]$	6	1839	157			
$\text{K}_2[\text{RuCl}_5\text{NO}]$	6	1843	176.7	1.738	1.131	[14]
$[\text{Co}(\text{NO})(\text{diars})_2]^{2+}$	8	1852	179			
$[\text{Ru}(2-\text{phpy})(\text{trpy})\text{NO}](\text{PF}_6)_2$	6	1858	167.1	1.826	1.139	[15]
$[\text{Ru}(\text{bpb})(\text{Cl})\text{NO}](\text{ClO}_4)_3$	6	1867	172.37	1.7534	1.1444	[16]
$\text{trans-}[\text{Ru}(\text{OH})(\text{py})_4\text{NO}](\text{ClO}_4)_2$	6	1868	172.8	1.756	1.145	[17]
$\text{trans-}[\text{RuCl}(\text{cyclam})\text{NO}](\text{ClO}_4)_2$	6	1875	178	1.747	1.128	[18]
$[\text{Fe}(\text{NO})(\text{diars})_2(\text{NCS})]^{2+}$	6	1885	180			
$[\text{Ru}(\text{HEDTA})\text{NO}]$	6	1890	172.3	1.756	1.156	[19]

[Fe('pyS ₄ ')NO]PF ₆	6	1893	179.5	1.634	1.141	[8]
[Fe(TpivPP)(NO ₂)NO]	6	1893	180	1.668	1.132	[20]
Na ₂ [Os(CN) ₅ NO]·2H ₂ O	6	1897	175.5	1.774	1.14	[21]
[Ru(NH ₃) ₅ NO]Cl ₃	6	1903	172.8	1.77	1.172	[22]
[Fe(cyclam-ac)NO](PF ₆) ₂	6	1904	175.5	1.663	1.132	[5]
trans-[RuCl(py) ₄ NO](ClO ₄) ₂	6	1910	172.9	1.766	1.123	[23]
[Fe(PaPy ₃)NO](ClO ₄) ₂	6	1919	173.1	1.677	1.139	[4]
[Fe(NO)(pyN ₄)] ³⁺	6	1926	180			
Na ₂ [Ru(CN) ₅ NO]·2H ₂ O	6	1926	173.9	1.776	1.127	[24]
trans-[Ru(NH ₃) ₄ (nic)NO] ₂ (SiF ₆) ₃	6	1940	177	1.71	1.17	[25]
Na ₂ [Fe(CN) ₅ NO]·2H ₂ O	6	1945	176.03	1.6656	1.1331	[26]
[Ru(dpk)(trpy)NO](ClO ₄) ₃	6	1949	173.1	1.764	1.126	[16]
K[IrCl ₅ NO]	6	1952	174.3	1.76	1.124	[27]
[Ru(bpy)(tpm)NO](ClO ₄) ₃	6	1959	179.1	1.774	1.093	[28]

x = number of {Fe(NO)_n}^x valence electrons; pybuS₄ = 2,6-bis(3,5-di(tBu)-2-mercaptophenylthio)methylene-pyridine(2-); PPh₃ = triphenylphosphine; salen = 2,2'-Ethylenebis(nitrilomethylidene)diphenol; diars = 1,2-Bis(dimethylarsino)benzene; Cyclam = 1,4,8,11-tetraazacyclotetradecane; oep = octaethylporphyrin; l-Melm = 1-methylimidazole; nic = nicotinamide; Phpy = 2-phenylpyridine; dpk = 2,2'-dipyridylketone; trpy = 2,2':6',2''-terpyridine; HEDTA = ethylenediaminetetraacetic acid, monoprotonated; tpm = trispyrazolylmethane.

References

- [1] Sellmann D, Gottschalk-Gaudig T et al (2001) [Ru(HNO)('py(bu)S₄')], the first HNO complex resulting from hydride addition to a NO complex ('pybuS₄'²⁻=2,6-Bis(2-mercaptop-3,5-di-tert-butylphenylthio)dime thylpyridine(2-1)). Chemistry 7:2099–2103
- [2] Sellmann D, Gottschalk-Gaudig T et al (2001) [Ru(HNO)(GÇ-pybuS₄GÇ-)], the First HNO Complex Resulting from Hydride Addition to a NO Complex (GÇ-pybuS₄GÇ-2GÇl=2,6-Bis(2-mercaptop- 3,5-di-tert-butylphenylthio)dimethylpyridine(2GÇl)). Chem Eur J 7:2099–2103
- [3] Melenkivitz R, Hillhouse GL (2002) Synthesis, structure, and reactions of a nitroxyl complex of iridium(III), cis,trans-IrHCl₂(NH=O)(PPh₃)₂. Chem Commun (Camb) 660–661
- [4] Patra AK, Rowland JM et al (2003) Iron nitrosyls of a pentadentate ligand containing a single carboxamide group: syntheses, structures, electronic properties, and photolability of NO. Inorg Chem 42:6812–6823
- [5] Serres RG, Grapperhaus CA et al (2004) Structural, spectroscopic, and computational study of an octahedral, non-heme [Fe-NO](6–8) Series: [Fe(NO)(cyclam-ac)]₂^{+/+0}. J Am Chem Soc 126:5138–5153
- [6] Lopez JP, Heinemann FW et al (2002) Iron carbonyl, nitrosyl, and nitro complexes of a tetrapodal pentadentate amine ligand: synthesis, electronic structure, and nitrite reductase-like reactivity. Chemistry 8:5709–5722
- [7] Wyllie GR, Schulz CE, Scheidt WR (2003) Five- to six-coordination in (nitrosyl)iron(II) porphyrinates: effects of binding the sixth ligand. Inorg Chem 42:5722–5734
- [8] Sellmann D, Blum N et al (2001) Synthesis, reactivity, and structure of strictly homologous 18 and 19 valence electron iron nitrosyl complexes. Chemistry 7:1874–1880
- [9] Nasri H, Ellison MK et al (1997) Sharing the $\pi\text{-C}$ -Bonding. An Iron Porphyrin Derivative with Trans, $\pi\text{-C}$ -Accepting Axial Ligands. Synthesis, EPR and M+Ässbauer Spectra, and Molecular Structure of Two Forms of the GÇéComplexGÇéNitronitrosyl(+,-,+,-,+--tetrakis(o-pivalamidophenyl)- porphinato)ferrate(II). Journal of the American Chemical Society 119:6274–6283
- [10] Ellison MK, Scheidt WR (1998) Tilt/Asymmetry in Nitrosyl Metalloporphyrin Complexes: The Cobalt Case. Inorg Chem 37:382–383
- [11] Li M, Bonnet D et al (2002) Tuning the electronic structure of octahedral iron complexes [FeL(X)] (L = 1-alkyl-4,7-bis(4-tert-butyl-2-mercaptopbenzyl)-1,4,7-triazacyclononane, X = Cl, CH(3)O, CN, NO). The S = 1/2 <=>3/2 Spin equilibrium of [FeL(Pr)(NO)]. Inorg Chem 41:3444–3456

- [12] Pohl K, Wieghardt K et al (1987) Preparation and magnetism of the binuclear iron(II) complexes $[\{Fe(C_9H_{21}N_3)X_2\}_2]$ ($X = NCS$, NCO , or N_3) and their reaction with NO. Crystal structures of $[\{Fe(C_9H_{21}N_3)(NCS)_2\}_2]$ and $[\{Fe(C_9H_{21}N_3)(NO)(N_3)\}_2]$. *J Chem Soc , Dalton Trans* 0:187–192
- [13] Singh P, Sarkar B et al (2006) The Metal–NO Interaction in the Redox Systems $[Cl_5Os(NO)]n^-$, $n = 1$ or 3 , and cis- $[(bpy)_2ClOs(NO)]^{2+/-}$: Calculations, Structural, Electrochemical, and Spectroscopic Results. *Inorg Chem* 45:4602–4609
- [14] Veal JT, Hodgson DJ (1972) The crystal and molecular structure of potassium pentachloronitrosylruthenate(II), $K_2[Ru(NO)Cl_5]$. *Acta Cryst B* 28:3525–3529
- [15] Hadadzadeh H, DeRosa MC et al (2002) Cyclometalated Ruthenium Chloro and Nitrosyl Complexes. *Inorg Chem* 41:6521–6526
- [16] Patra AK, Rose MJ et al (2004) Photolabile ruthenium nitrosyls with planar dicarboxamide tetridentate N(4) ligands: effects of in-plane and axial ligand strength on NO release. *Inorg Chem* 43:4487–4495
- [17] Togano T, Kuroda H et al (1992) Synthesis, properties and molecular structure of trans-hydroxobis(2,2'-bipyridine)nitrosylruthenium(2+): influence of axial ligand on characteristics of nitrosyl moiety in trans- $[Ru(NO)XL_4]n^+$ ($X=OH, Cl$; $L=py, 1/2(bpy)$) type complexes. *Inorganica Chimica Acta* 196:57–63
- [18] Lang DR, Davis JA et al (2000) A Controlled NO-Releasing Compound: Synthesis, Molecular Structure, Spectroscopy, Electrochemistry, and Chemical Reactivity of R,R,S,S-trans-[RuCl(NO)(cyclam)] $^{2+}(1,4,8,11$ -tetraazacyclotetradecane). *Inorg Chem* 39:2294–2300
- [19] Zanichelli PG, Miotto AM et al (2004) The $[Ru(Hedta)NO](0.1^-)$ system: structure, chemical reactivity and biological assays. *J Inorg Biochem* 98:1921–1932
- [20] Ellison MK, Schulz CE, Scheidt WR (1998) Syntheses, Characterization, and Structural Studies of Several (Nitro)(nitrosyl)iron(III) Porphyrinates: $[Fe(Porph)(NO_2)(NO)]$. *Inorg Chem* 38:100–108
- [21] Baraldo LM, Bessegga MS et al (1994) Crystal and Molecular Structure, Spectroscopic Properties, and Electrophilic Reactivity of Sodium Pentacyanonitrosylsmate(II) Dihydrate. *Inorg Chem* 33:5890–5896
- [22] Bottomley F (1974) Reinvestigation of the crystal and molecular structures of penta-amminenitrosylruthenium trichloride hydrate and trans-tetra-ammine-hydroxonitrosylruthenium dichloride. *J Chem Soc , Dalton Trans* 0:1600–1605
- [23] Kimura T, Sakurai T et al (1983) Structure of trans-chloronitrosyltetrakis(pyridine)ruthenium(II) bis(hexafluorophosphate) hemihydrate. *Inorganica Chimica Acta* 69:135–140
- [24] Olabe JA, Gentil LA et al (1984) Crystal and molecular structure of sodium pentacyanonitrosylruthenate(II) dihydrate and its spectroscopic properties and reactivity. *Inorg Chem* 23:4297–4302
- [25] Borges Sd, Davanzo CU et al (1998) Ruthenium Nitrosyl Complexes with N-Heterocyclic Ligands. *Inorg Chem* 37:2670–2677
- [26] Carducci MD, Pressprich MR, Coppens P (1997) Diffraction Studies of Photoexcited Crystals: Metastable Nitrosyl-Linkage Isomers of Sodium Nitroprusside. *Journal of the American Chemical Society* 119:2669–2678
- [27] Bottomley F, Clarkson SG, Tong SB (1974) Electrophilic behaviour of the co-ordinated nitrosyl cation: reactions of pentahalogenonitrosyliridate(1-). *J Chem Soc , Dalton Trans* 0:2344–2346
- [28] Videla M, Jacinto JS et al (2006) New ruthenium nitrosyl complexes with tris(1-pyrazolyl)methane (tpm) and 2,2'-bipyridine (bpy) coligands. Structure, spectroscopy, and electrophilic and nucleophilic reactivities of bound nitrosyl. *Inorg Chem* 45:8608–8617