Electronic Supplementary Information

Ferromagnetic versus antiferromagnetic exchange in oximate nickel(II) complexes

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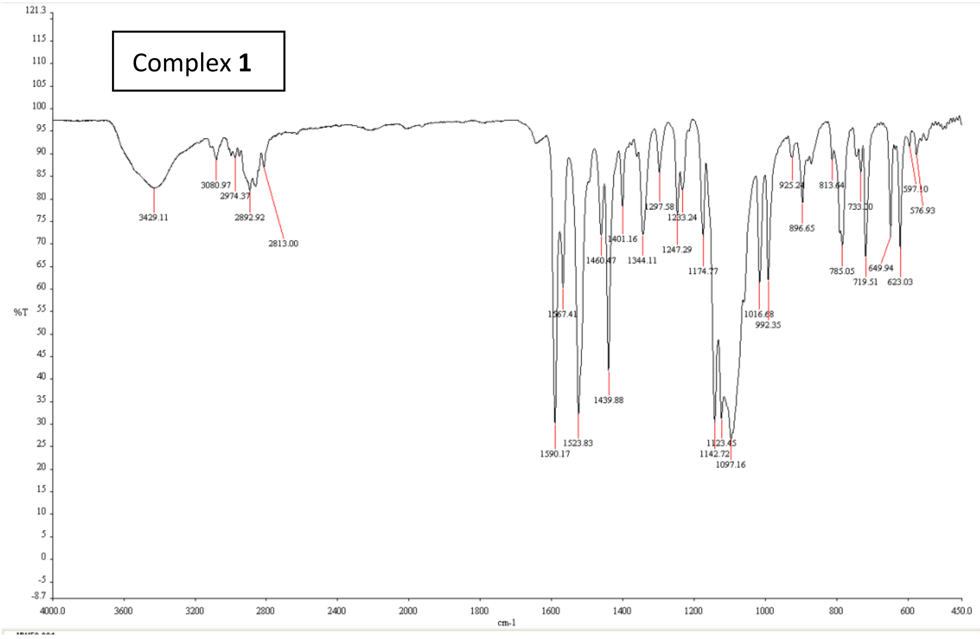
Complex **1**
%T
cm-1
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3080.97
2974.37
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1590.17
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1523.83
1460.47
1439.88
1401.16
1344.11
1297.58
1253.24
1247.29
1174.77
1142.72
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1097.16
1016.68
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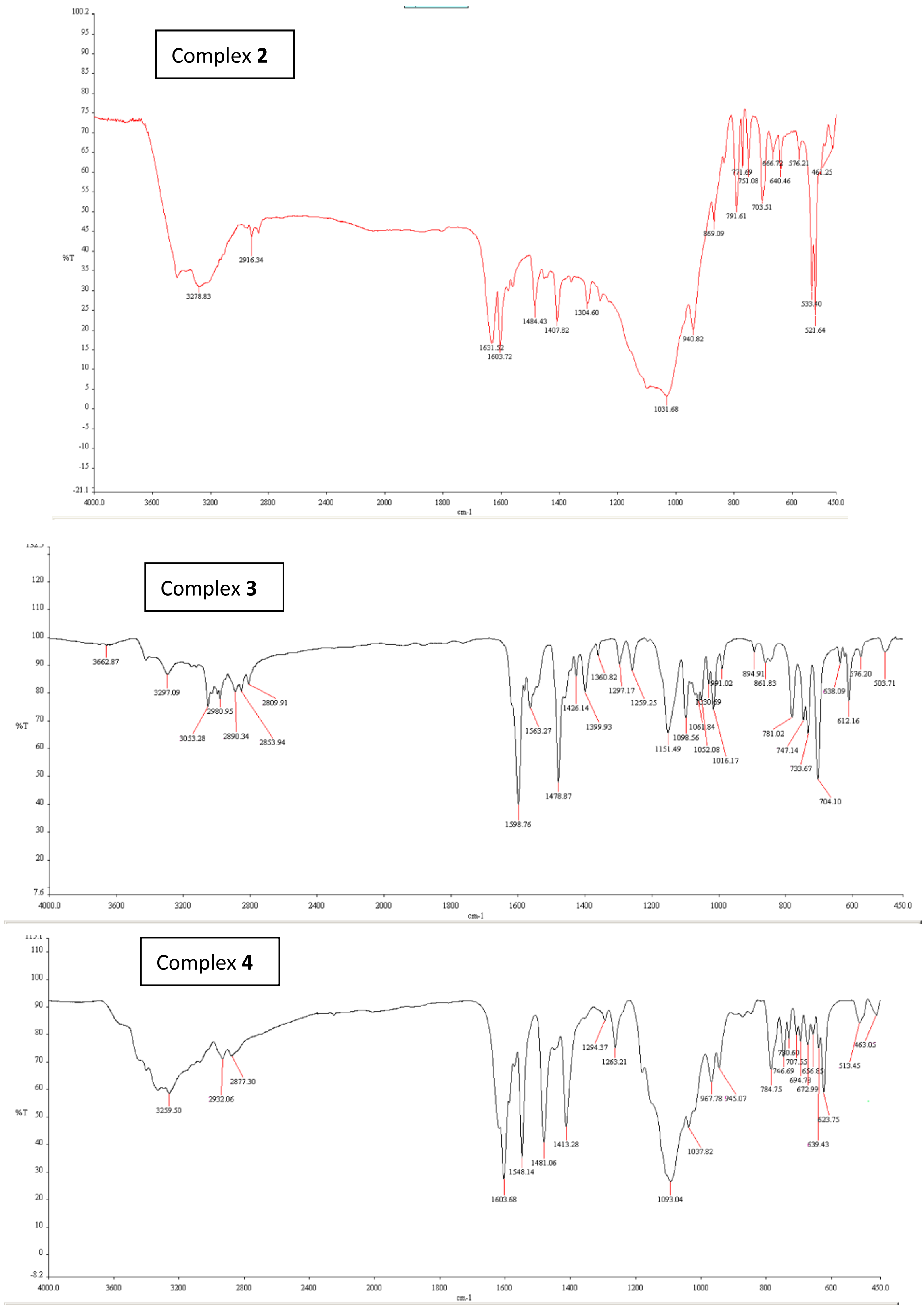
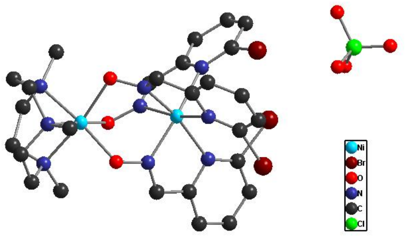
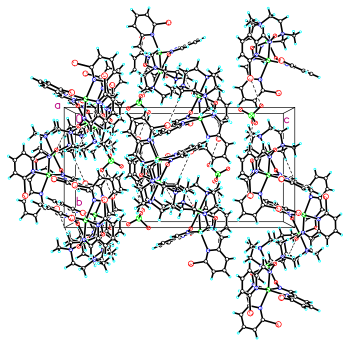
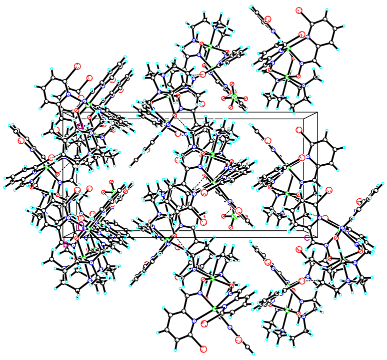


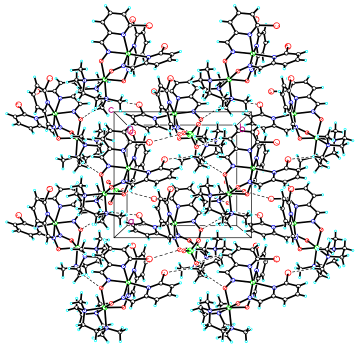
Fig. S1. Infrared spectra for complexes **1-4**.





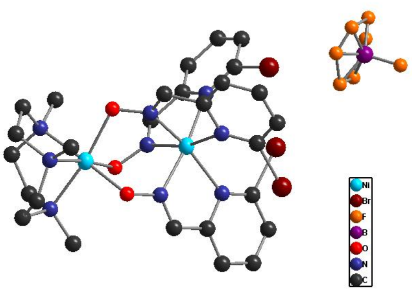
（a）　　　　　　　　（b）

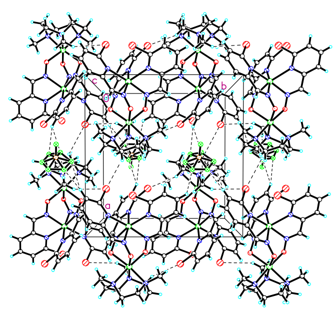




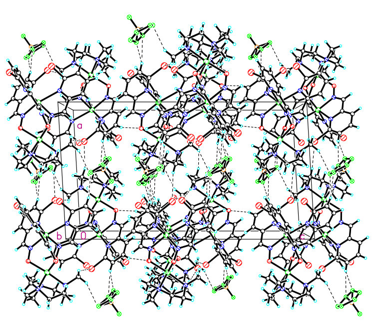
（c）　　　　　　　　（d）

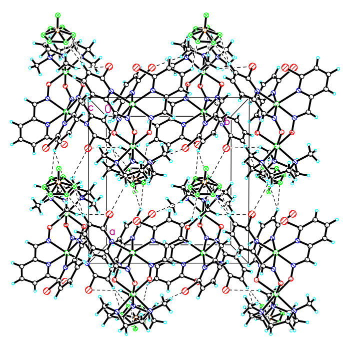
Fig. S2. (a) Top view of the molecular structure of the complex **1**. (b-d) Cell packing diagrams along the a, b and c axis, respectively, showing the intermolecular hydrogen bonding interactions.





（a）　　　　　　　　（b）





（c）　　　　　　　　（d）

Fig. S3. (a) Top view of the molecular structure of the complex 2. (b-d) Cell packing diagrams along the a, b and c axis, respectively, showing the intermolecular hydrogen bonding interactions.

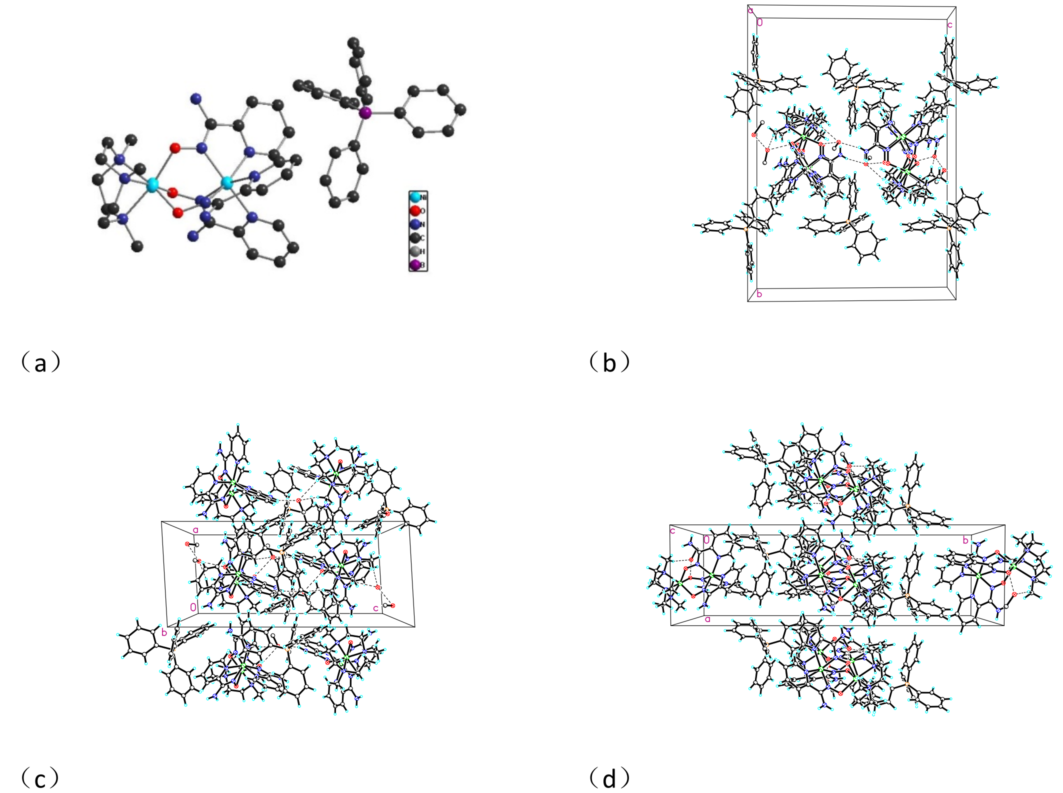


Fig. S4. (a) Top view of the molecular structure of the complex 3. (b-d) Cell packing diagrams along the a, b and c axis, respectively, showing the intermolecular hydrogen bonding interactions.

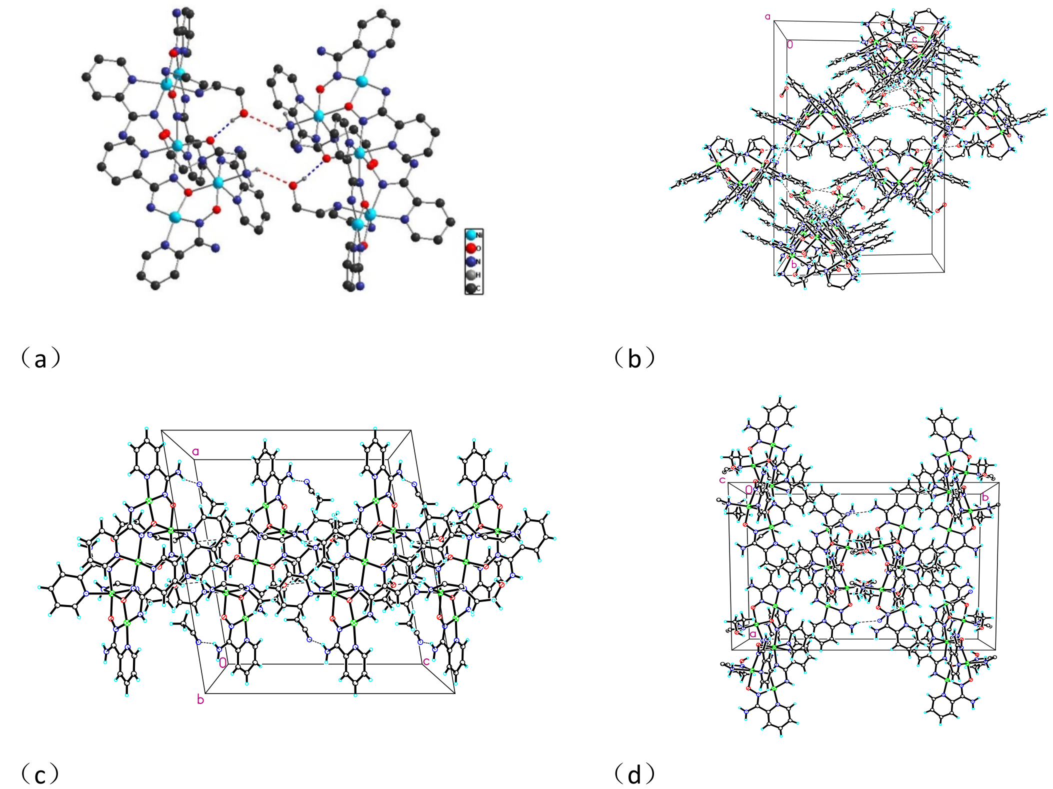


Fig. S5. (a) Intra- and inter-molecular hydrogen bond in complex **4**. (b-d) Cell packing diagrams along the *a*, *b* and *c* axis, respectively, showing the intermolecular hydrogen bonding interactions.

Table S1. Comparison of structural and magnetic coupling via the N-O bridges for oximato-bridged Ni(II) complexes

Compounds	J/cm^{-1}	$d_{N\text{-}O}$/Å	Torsion angle/°	ref
$K_4[Ni(H_2O)_6][Ni_8(Hvi)_{10}(H_2vi)_2]$	-30	0.932-1.265	166.63-177.67	24
$Ni_2(moda)_2(Odien)_2](ClO_4)_2$	-32.0	1.310	7.05	19
$[Ni_2(pao)_3(Me_3tacn)]ClO_4$	-33.6	1.326(3)–1.338(3)	41.3–44.3	15
$[Ni_2(tren(DO))_2](ClO_4)_2$	-39.5	1.327,1.347	23.38, 34.63	27
$[Ni_5Br_3(MeO)_4(pyC\{CN\}NO)_3(MeOH)_6]$	-25.7	1.312(3)	38.3(3)	26
$[Ni_4(L^1)_4Cl_2(MeOH)_2](ClO_4)_2$	-11.1	1.395(4)	38.2, 39.7, 70.9, 71.2	23
$[Ni_4(L^1)_4(N_3)_2(MeOH)_2](ClO_4)_2$	-11.4	1.388(2), 1.392(2)	34.2, 41.3, 68.5, 73.0	23
$[Ni_4(L^2)_4(pyz)_2(PhCOO)_2(MeOH)_2]$-$(ClO_4)_2$	-5.4	1.391(2), 1.395(3)	41.5, 41.7, 68.3, 69.0	23
$[Ni_3(Dtox)(DtoxH)_2](ClO_4)_2$	-7.6(11)	1.391(5), 1.394(5)	69.5, 75.7	29
$[Ni_2(HL^3)_2](ClO_4)_2$	-12	1.388(4)	70.4	20
$[Ni_4(HL^4)_2(AcO)_2(MeOH)]$	-16	1.378(3)	132.7	28
$[Ni_2(Br\text{-}pao)_3(Me_3tacn)]ClO_4$ (**1**)	-16.7	1.324(8)-1.337(9)	47.2-50.4	This work
$[Ni_2(Br\text{-}pao)_3(Me_3tacn)]BF_4$ (**2**)	-17.7	1.324(1)-1.341(8)	45.6-51.9	This work
$[Ni_2(Hpyaox)_3(Me_3tacn)]BPh_4$ (**3**)	-18.5	1.371(3)-1.377(3)	38.3-40.9	This work
$[Ni_4(dpt)_2(N_3)_4(py_2CNO)_4]$	-14.4	1.330(2)	18.0(2)	25
$[Ni_5(3\text{-}ClBzO)_2(dapdo)_2(Hdapdo)_2$-$(dca)_2(MeOH)_2]$	-0.25(10)	1.385(2)	103.3(2)	21
$[Ni_4(Hpzaox)_2(pzaox)_2(H_2O)_2](NO_3)_2$	-0.35(5)	1.383(12)	2.23	10
$[Ni_4(AcO)_3(dapdo)(Hdapdo)_2(H_2O)_3]$-$(AcO)$	+0.58	1.387(4)	92.5(2)	22
$[Ni_4(Hpyaox)_2(pyaox)_2(Him)_4](ClO_4)_2$	+1.9	1.413(10)	2.8	8
$[Ni_4(Hpyaox)_2(pyaox)_2(py)_4](ClO_4)_2$	+1.6	1.410(3)	10.55	11
$[Ni_5(Hpyaox)_4(pyaox)_2L_2](ClO_4)_2$ (**4**)	+3.12	1.404(5), 1.365(5)	8.3(5), 75.7(4)	This work
$[Ni_4(Hpyaox)_2(pyaox)_2(4\text{-}CH_3py)_4](ClO_4)_2$	+3.4	1.418(8)	13.41	11
$[Ni_4(Hpyaox)_2(pyaox)_2(3\text{-}CH_3py)_4](ClO_4)_2$	+6.3	1.411(5), 1.419(5)	10.05, 11.32	11
$Ni_4(Hpyaox)_2(pyaox)_2(1\text{-}CH_3im)_4](ClO_4)_2$	+2.28	1.395(3)	7.96	11
$[Ni_4(Hpzaox)_2(pzaox)_2(py)_4](ClO_4)_2$	+1.19(5)	1.409(4)	5.15	10
$[Ni_4(Hpzaox)_2(pzaox)_2(py)_4](NO_3)_2$	+4.8(2)	1.402(4)	0	10
$[Ni_8(Hpyaox)_4(pyaox)_4(H_2O)_4]Br_4$	+0.442	1.420(13), 1.415(15)	18.70, 18.40	11
$[Ni_8(Hpyaox)_4(pyaox)_4(Him)_4](NO_3)_2(OH)_2$	+2.03	1.417(11), 1.460(11)	11.32, 2.80	11

$[Ni_{12}(Hpyaox)_6(pyaox)_6(H_2O)_2]Cl_6$	+1.04	1.400(6), 1.417(6), 1.427(6)	11.06, 12.31	11
$[Ni_8(Hpyaox)_4(pyaox)_4(H_2O)_4](ClO_4)_2$	+3.10	1.404(4)–1.418(4)	16.2–21.1	8
$[Ni_{12}(Hpyaox)_6(pyaox)_6(H_2O)_2(N_3)_2](ClO_4)_4$	+0.24	1.401(8)-1.429(8)	0.8–15.5	8
$[Ni_{12}(Hpyaox)_6(pyaox)_6(MeOH)_2Cl_2]Cl_4$	+2.28	1.393(5)-1.412(5)	11.2–19.8	9

H_3vi, 5-(hydroxyimino)-2,4,6-(1H,3H,5H)-pyrimidinetrione; Hmoda, 2,3-butanedione monoxime; Odien, 1,5-diamino-3-oxapentane; Me_3tacn, 1,4,7-trimethyl-1,4,7-triazacyclononane; pao$^-$, anion of pyridine-2-aldoxime; Htren(DO), 1:1 Schiff base from 2,3-butanedione monoxime and tris[2-aminoethyl]amine; 4-CH_3py, 4-methylpyridine; 3-CH_3py, 3-methylpyridine; HL^1, bipyridine-2-carboxamideoxime; HL^2, pyrimidine-2-carboxamideoxime; DtoxH$_2$, 4,7-dithiadecane-2,9-dione dioxime; H_2L^3, 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dioxime; H_4L^4, N,N'-dimethyl-N,N'-ethylene-bis(5-bromo-3-formyloxime-2-hydroxybenzylamine; H_2dapdo, 2,6-diacetylpyridine dioxime; dpt, dipropylenetriamine; Hpy$_2$CNO, dipyridylketoneoxime; HpyC{CN}NO, 2-pyridylcyanoxime; H_2pzaox, pyrazine-2-amidoxime.

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