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METAL CYANONITROSYL COMPLEXES: SYNTHESIS, MAGNETIC AND SPECTRAL STUDIES OF SOME NOVEL MIXED-LIGAND CYANONITROSYL $\{CoNO\}_8$ COMPLEXES OF COBALT(I) WITH HETEROCYCLIC BASES

R. C. MAURYA,* D. D. MISHRA, S. MUKHERJEE and J. DUBEY

Coordination Chemistry Laboratory, Department of P.G. Studies and Research in Chemistry, R. D. University, Jabalpur 482 001, India

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Abstract—Novel mixed-ligand cyanonitrosyl complexes of cobalt(I), formed by the interaction of $K_2[Co(NO)(CN)_4(H_2O)] \cdot H_2O$ with some heterocyclic bases, namely nicotinamide, *N*-methylnicotinamide, *N*-hydroxymethylnicotinamide, pyridine-2-aldoxime, pyridine-3-aldoxime, pyridine-4-aldoxime, 2-hydroxymethylpyridine, 3-hydroxymethylpyridine and 4-hydroxymethylpyridine, have been prepared. The products, characterized by elemental analyses, molar conductances, magnetic measurements, EPR, ^{1}H NMR and IR spectral studies, UV–vis and thermogravimetric analysis, have the general formula $K_2[Co(NO)(CN)_4(L)] \cdot H_2O$ (where L = the above ligands), for which a tetragonally distorted octahedral structure has been proposed. The overall IR spectral studies suggest that all the heterocyclic bases act as neutral monodentate ligands coordinating through the ring nitrogen. Cobalt(I) has a low-spin $\{CoNO\}^8$ electron configuration (J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.* 1974, 13, 339) in these diamagnetic complexes, which behave as 2 : 1 electrolytes.

The chemistry of cyanonitrosyl complexes of cobalt is still not well understood. Nitric oxide, which is an odd electron molecule, can form coordination compounds in four different ways:[1] (i) by loss of the odd electron followed by the coordination of the resultant NO^+ species, (ii) by the gain of an electron followed by the coordination of the resultant NO^- species, (iii) by coordination of the neutral NO group, and (iv) by bonding of the NO group in a bridging position, N═O, similar to CO with the metal atom. The cyano derivatives are among the most frequently encountered anionic nitrosyls and since the cyanide ion has one of the largest capacities for inducing spin pairing in transition metal complexes, the majority of complexes are either diamagnetic or have low magnetic moments. Very few reports are available regarding the preparation of cyanonitrosyl complexes of cobalt. Nast and Rohmer[2] reported the preparation of a yellow compound, $K_3[Co^{III}(NO^-)(CN)_5] \cdot 2H_2O$, by the reaction of $[Co^{III}(NO^-)(NH_3)_5]Cl_2$ with excess of KCN and KOH. Detailed studies of such compounds have been carried out by Wilkinson *et al.*[3] and Zhilinskaya and co-workers using UV–vis,[4] IR[5] and X-ray[6] techniques. NMR studies of these compounds have been done by Suvorov *et al.*[7]

In the present investigation, potassium monoaquatetracyanonitrosylcobaltate(I) mohonydrate, $K_2[Co^I(NO)(CN)_4(H_2O)] \cdot H_2O$, has been prepared and was reacted with some heterocyclic bases, namely nicotinamide (NA, **I**), *N*-methylnicotinamide (NMNA, **II**), *N*-hydroxymethylnicotinamide (NHMNA, **III**), pyridine-2-aldoxime (2-PA, **IV**), pyridine-3-aldoxime (3-PA, **V**), pyridine-4-aldoxime (4-PA, **VI**), 2-hydroxymethylpyridine (2-HMPY, **VII**), 3-hydroxymethylpyridine (3-HMPY, **VIII**) and 4-hydroxymethylpyridine (4-HMPY, **IX**), in aqueous ethanol medium. The products so obtained have been characterized by different physico-chemical tech-

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* Author to whom correspondence should be addressed.

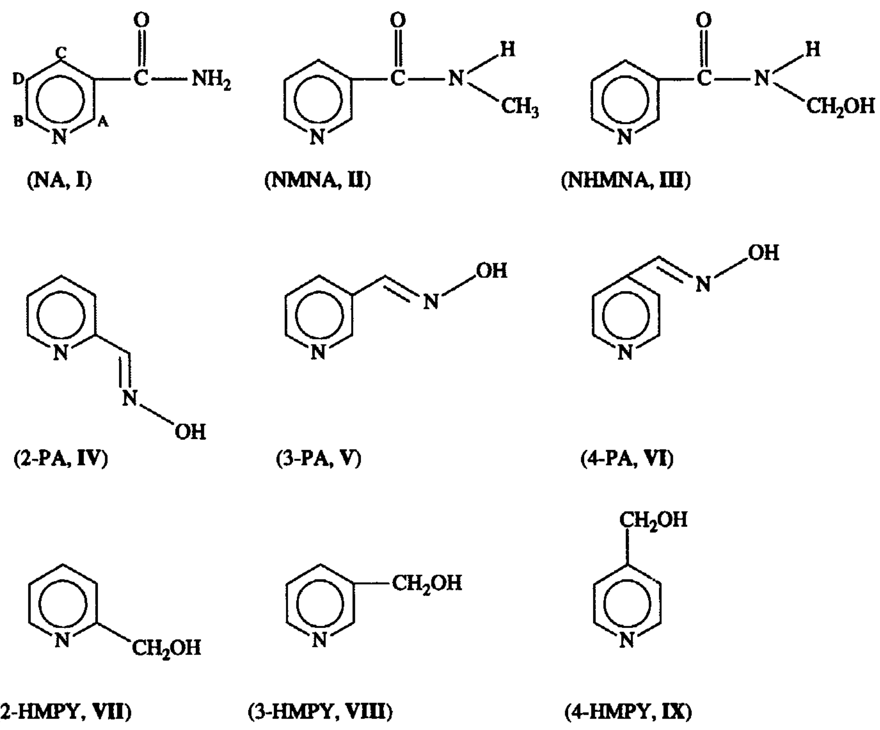


Fig. 1.

niques. The structures of the heterocyclic bases are shown in Fig. 1.

EXPERIMENTAL

Materials

2-PA, 3-PA, 4-PA (Aldrich Chem. Co., U.S.A.), NA (Parke Davis, India), NMNA (Sisco, Bombay), NHMNA (Wilson Laboratories, Bombay), 2-HMPY, 3-HMPY, 4-HMPY (Kawaken Fine Chemicals Co. Ltd., Japan), 2- and 3-cyanopyridine (Nepera, Inc, New York), potassium cyanide (May & Baker Co., India), cobaltous nitrate (Ranbaxy Laboratories Ltd., India) and hydroxylammonium chloride (Robert Johnson, India) were used as supplied.

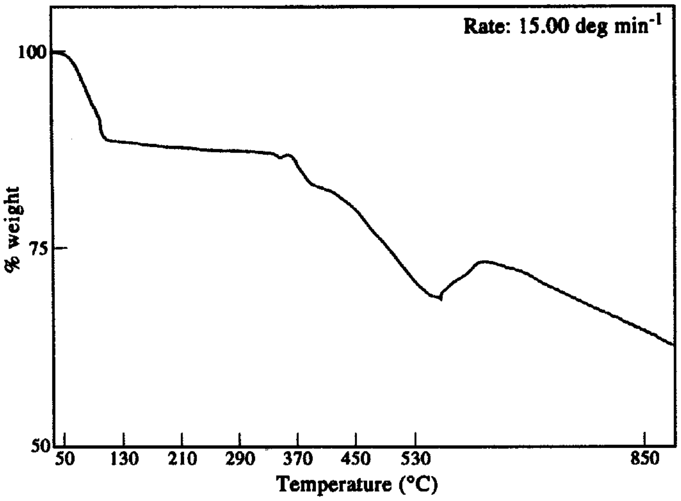
Preparation of the parent compound

The parent compound, potassium monoaquatetracyanonitrosylcobaltate(I) monohydrate, was prepared by following the procedure reported elsewhere.[8]

A solution containing 0.1 mol (6.5 g) of potassium cyanide was maintained at 5 ± 1°C in a 150 cm^3 beaker, pure nitrogen was then bubbled through the solution for 30 min and then an aqueous solution (30 cm^3) of cobalt(II) nitrate hexahydrate (0.015 mol, 4.48 g) was added dropwise. During the course of addition of the two solutions, a yellowish-green solution of $K_3[Co(CN)_5]$ was formed.[9] Then solutions of KOH (0.017 mol, 1 g) in water and $NH_2OH \cdot HCl$ (0.01 mol, 0.69 g) in ethanol were added simultaneously. The contents were thoroughly stirred for 1 h and then heated on a water bath for 30 min. The nitrogen bubbling was continued throughout the reaction. The solution was cooled and filtered, then the filtrate was poured with stirring into 80% methanol. The precipitate so obtained was filtered and dissolved in distilled water. It was again precipitated with methanol. The precipitate was dried *in vacuo* over anhydrous calcium chloride, yield 50%, yellow. Found: C, 15.3; H, 1.5; N, 22.4; Co, 18.9. Calc. for $K_2C_4H_4N_5O_3Co$: C, 15.6; H, 1.3; N, 22.8; Co, 19.2%. IR: ν(CN) 2129, ν(NO) 1625 and ν(OH) 3550–3380 cm^{-1}. δ(HOH) seems to be merged with the nitrosyl peak. A weight loss observed by TGA at 120°C in the parent compound corresponds to elimination of two molecules of water and further supports the presence of one molecule of coordinated water[10] (Fig. 2a).

Preparation of the mixed-ligand complexes

To the filtered aqueous solution (40 cm^3) of the parent compound, $K_2[Co(NO)(CN)_4(H_2O)] \cdot H_2O$



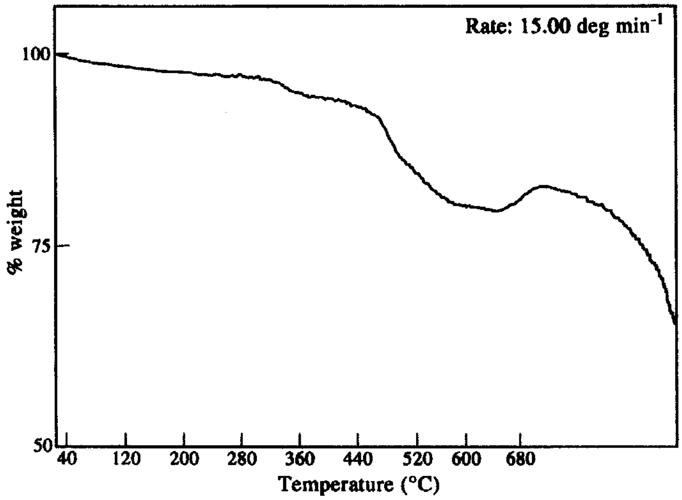


Fig. 2.(a) TGA curve of the parent compound, $K_2[Co(NO)(CN)_4H_2O]\cdot H_2O$. (b) TGA curve of compound **1**, $K_2[Co(NO)(CN)_4(NA)]\cdot H_2O$.

(0.01 M), an alcoholic solution (15 cm^3, 0.01 M) of the corresponding ligand was added with shaking. The resulting yellowish solution was refluxed for 3–4 h over a hot plate at 80°C when a white solid was precipitated, which was filtered by suction, washed several times with alcohol and dried *in vacuo* over anhydrous $CaCl_2$ at room temperature. The yields were 35–80%. The analytical data are given in Table 1.

Analyses

Carbon, hydrogen and nitrogen were determined microanalytically. Cobalt in the complexes was determined gravimetrically as $CoSO_4$[11] after igniting the complexes and treating the residue with conc. HNO_3 and H_2SO_4.

Physical methods

The magnetic susceptibility measurements were made at room temperature by the Gouy method. The apparatus was calibrated using mercury(II) tetrathiocyanatocobaltate(II), $Hg[Co(NCS)_4]$. IR spectra of the complexes were recorded in Nujol mulls on a Perkin–Elmer 457 grating IR spectrometer. The ^1H NMR spectra were recorded on an EM-390 90MHZ NMR spectrometer; EPR was recorded at 298 K on a Bruker spectrometer. Room temperature molar conductivities in 10^{-3} M solutions in DMF were measured on a Toshniwal conductivity bridge fitted with a dip-type cell, having platinum electrodes (cell constant 1.3 cm^{-1}). TG curves were recorded on a Perkin–Elmer instrument at a heating rate of 15°C min^{-1}. Electronic spectra were recorded on a Shimadzu model UV-160 spectrophotometer.

Table 1. Analytical data, physical properties, IR, ^{1}H NMR and UV–vis data of the complexes

Structure no.	Ligand complex	Found (Calc.) (%)				$\nu(NO)^+$	ν(Co—NO)	$\nu(CN)^a$	UV–vis data λ_{max} (nm)		^{1}H NMR^b (ppm)
		Co	C	H	N						
I	NA								256 239		
1	$K_2[Co(NO)(CN)_4(NA)]\cdot H_2O$	14.1 (14.3)	29.4 (29.2)	2.1 (1.9)	23.6 (23.8)	1630	630	2129 (S) 2150 (sh)	312 257 220	H_A H_B H_C H_D	9.35 (s, 1H) 9.1 (d, 1H) 9.25 (d, 1H) 7.60 (t, 1H)
II	NMNA								236 254		
2	$K_2[Co(NO)(CN)_4(NMNA)]\cdot H_2O$	13.6 (13.9)	31.2 (31.0)	2.0 (2.3)	23.2 (23.0)	1625	615	2130 (S) 2145 (sh)	310 254 219	H_A H_B H_C H_D	9.3 (s, 1H) 9.0 (d, 1H) 9.2 (d, 1H) 7.58 (t, 1H) 2.3 (s,3H)
III	NHMNA								255 238		
3	$K_2[Co(NO)(CN)_4(NHMNA)]\cdot H_2O$	13.1 (13.4)	29.6 (29.9)	2.4 (2.2)	22.5 (22.2)	1628	617	2128 (S) 2140 (sh)	312 256 218	H_A H_B H_C H_D	9.4 (s, 1H) 9.1 (d, 1H) 9.23 (d, 1H) 7.62 (t, 1H) 2.6 (s, 2H)
IV	2-PA								261 235		
4	$K_2[Co(NO)(CN)_4(2\text{-}PA)]\cdot H_2O$	14.1 (14.3)	29.0 (29.2)	1.7 (1.9)	23.7 (23.8)	1630	590	2128 (S) 1085 (sh)	309 257 218	H_B H_C H_D H_D	9.15 (d, 1H) 7.62 (d, 1H) 7.10 (t, 1H) 7.3 (d, 1H) 3.9 (s, 1H)
V	3-PA								261 235		
5	$K_2[Co(NO)(CN)_4(3\text{-}PA)]\cdot H_2O$	14.6 (14.3)	29.4 (29.2)	1.8 (1.9)	23.6 (23.8)	1625	570	2129(S) 2090 (sh)	309 257 218	H_A H_B H_C H_D	9.32 (s, 1H) 9.15 (d, 1H) 7.4 (d, 1H) 7.1 (t, 1H) 3.8 (s, 1H)

Table 1—*continued.*

											9.9 (s, 1H)
VI	4-PA								261		
									235		
6	$K_2[Co(NO)(CN)_4(4\text{-}PA)]\cdot H_2O$	14.6	29.4	2.1	23.6	1630	565	2129(S)	309	H_A	9.28 (d, 1H)
		(14.3)	(29.2)	(1.9)	(23.8)			2094 (sh)	257	H_B	9.15 (d, 1H)
									218	H_D	7.2 (d, 1H)
											3.8 (s, 1H)
											10 (s, 1H)
VII	2-HMPY								256		
									237		
7	$K_2[Co(NO)(CN)_4(2\text{-}HMPY)]\cdot H_2O$	14.5	30.3	2.0	21.3	1625	620	2128 (S)	310	H_B	9.1 (d, 1H)
		(14.8)	(30.1)	(2.2)	(21.1)			2100 (sh)	257	H_C	7.45 (d, 1H)
									219	H_D	7.2 (t, 1H)
										H_D	7.1 (d, 1H)
											3.15 (s, 2H)
											2.4 (s, 1H)
VIII	3-HMPY								256		
									236		
8	$K_2[Co(NO)(CN)_4(3\text{-}HMPY)]\cdot H_2O$	14.9	30.3	2.0	21.3	1630	617	2130 (S)	309	H_A	9.2 (s, 1H)
		(14.8)	(30.1)	(2.2)	(21.1)			2101 (sh)	256	H_B	9.4 (d, 1H)
									218	H_C	7.4 (d, 1H)
										H_D	7.1 (t, 1H)
											3.1 (s, 2H)
											2.5 (s, 1H)
IX	4-HMPY								257		
									238		
9	$K_2[Co(NO)(CN)_4(4\text{-}HMPY)]\cdot H_2O$	14.7	30.3	2.0	21.2	1625	625	2135 (S)	312	H_A	9.21 (d, 1H)
		(14.8)	(30.1)	(2.2)	(21.1)			2105 (sh)	256	H_B	9.31 (d, 1h)
										H_D	7.2 (d, 1H)
										H_D	7.22 (d, 1H)
											3.2 (s, 2H)
											2.45 (s, 1H)

[a] S = strong; sh = shoulder band.

[b] **I–IX**, solvent is deuterium oxide; **1–9**, solvent is acetone-d_6. s = singlet, d = doublet, t = triplet.

RESULTS AND DISCUSSION

The mixed-ligand complexes of cobalt(I) were prepared according to the following equation:

$$K_2[Co(NO)(CN)_4(H_2O)] \cdot H_2O + L \xrightarrow[\text{Reflux}]{H_2O,\,C_2H_5OH} K_2[Co(NO(CN)_4(L)] \cdot H_2O$$

where L = NA, NMNA, NHMNA, 2-PA, 3-PA, 4-PA, 2-HMPY or 3-HMPY or 4-HMPY.

All the compounds are hydroscopic, cream yellow solids. They give a positive Griess reagent[12] test, i.e. the complexes, after decomposition with KOH, followed by acidifying with acetic acid, give a pink colour with a few drops of the Griess reagent. The appearance of the pink colour is due to the nitrosyl group (as NO^+) of the compounds which, after decomposition with KOH, changes to NO_2^- and forms a pink dye with the Griess reagent. They are thermally stable and their decomposition temperatures are above 320°C. The resulting compounds were characterized on the basis of the following physical studies.

IR spectra

The important IR spectral bands and their tentative assignments are given in Table 1. All the complexes exhibit characteristic bands at 1625–1630, 565–625 and 2128–2135 cm^{-1}, with a shoulder at 2085–2150 cm^{-1} which may be assigned to $\nu(NO)$,[13] $\nu(Co—NO)$[14] and $\nu(CN)$,[15] respectively. In the IR spectra of all the complexes, the $\nu(OH)$ bands appeared in the region 3600–3200 cm^{-1}, showing the presence of lattice water[16] in the complexes. The $\delta(HOH)$ appears to be merged with the broad nitrosyl peak in some complexes.

The ligands NA, NMNA, NHMNA, 2-PA, 3-PA and 4-PA used in the present study possess two donor sites: (i) the pyridine ring nitrogen and (ii) the amide oxygen in the case of NA, NMNA and NHMNA and the oxime group nitrogen in the case of 2-PA, 3-PA and 4-PA. The remaining three ligands, 2-HYMPY, 3-HMPY and 4-HMPY, contain only the pyridine ring nitrogen as the donor site. For the sake of convenience, the present discussion is divided into three parts.

Complexes of NA, NMNA and NHMNA

Significant IR absorption bands due to the amide group are $\nu(NH)$, $\nu(CO)$ and $\nu(CN)$. In the amides and other carbonyl donors, a significant shift to lower wavenumbers of the $\nu(CO)$ takes place because of the coordination through the carbonyl oxygen. The $\nu(NH)$, $\nu(CO)$ and $\nu(CN)$ frequencies of the uncoordinated NA, NMNA and NHMNA remain unperturbed in their respective complexes. These features clearly indicate that the amide oxygen is inert towards bonding. However, the ring $\nu(C{=}N)$ and pyridine ring breathing mode occurring at ~1570 and ~990 cm^{-1} in the free ligands undergo significant shifts to higher frequency in the complexes. These features indicate conclusively that coordination of these ligands takes place via their pyridine ring nitrogen[17] only.

Complexes of 2-*PA*, 3-*PA and* 4-*PA*

IR spectra of 2-PA, 3-PA and 4-PA complexes show bands due to the oxime group at almost the same positions as in the free aldoximes. This indicates that the oxime group is inert towards coordination in these ligands. In general, only small shifts in the vibrational frequencies of the pyridine rings are observed in the complexes of these ligands. However, the evidence of coordination of the pyridine ring nitrogen[18] in 2-PA, 3-PA and 4-PA is manifested by a significant shift to higher frequency of 15–20 cm^{-1} in the pyridine ring breathing mode occurring at ~995 cm^{-1} in the free aldoximes.

Complexes of 2-*HMPY*, 3-*HMPY and* 4-*HMPY*

The characteristic bands appearing in the complexes at 1590–1600 and 1015–1020 cm^{-1}, most probably due to the pyridine ring $\nu(C{=}N)$ and ring breathing mode, respectively, suggest the coordination of pyridine ring nitrogen[18] in these ligands.

Thermogravimetric analysis

TGA of the complexes was done to support the replacement of a water molecule in the parent compound by the reacting ligand. It was found that no weight loss for coordinated water was observed around 120°C in the case of the resulting complexes (Fig. 2b).

Electronic spectra

The electronic spectra of complexes were studied at a concentration of 1×10^{-4} M in distilled water. In the complexes a blue shift was observed (218–220 nm) for the ligand band in the range 235–239 nm. All the complexes show an additional band in the region 309–312 nm, which may be due to ligand to metal charge transfer transition.

^{1}H *NMR*

NMR spectra of the ligand and the complexes were recorded in D_2O and acetone-d_6, respectively. The chemical shifts of the various protons present in the ligand and in its respective complex suggest that the coordination takes place through the pyridine ring nitrogen. In the ligands **I–III, V, VI, VIII** and **IX**, the two adjacent protons H_A (8.5–9.13 ppm) and H_B (8.62–8.72 ppm) present on either side of the pyridine ring nitrogen undergo downfield shifts to 9.15–9.4 and 9–9.4 ppm, respectively. In ligands **IV** and **VII** only one adjacent proton, i.e. H_B (8.65 ppm), is deshielded to 9.1–9.15 ppm. The remaining protons do not undergo any change after complexation. As the solvent used is acetone-d_6 the signal for the NH_2 protons becomes merged with the solvent peak in complexes **1–3**. The signals for NH and OH protons were not observed due to the rapid exchange with the solvent D_2O; instead, a weak signal was observed around 4.8 ppm due to HOD absorption in ligands **I–IX**.

Conductance measurements

The observed molar conductances (205.6–218.5 ohm^{-1} cm^2 mol^{-1}) of all the complexes in 10^{-3} M DMF solution suggest that the resulting complexes are 2 : 1 electrolytes.[19]

Magnetic measurements

The magnetic susceptibility measurements of these complexes indicate that they are diamagnetic compounds. This result is consistent with a low-spin $\{CoNO\}^8$ electron configuration (Fig. 3) of cobalt(I) in all the complexes.[20] The diamagnetic and 2 : 1 electrolytic nature of these complexes also support the presence of the nitrosyl grouping as NO^+ in these complexes.

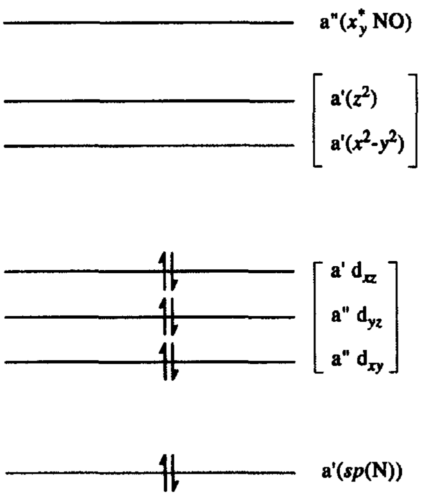


Fig. 3.

EPR studies

All the cobalt(I) mixed-ligand complexes were found to be diamagnetic in nature by EPR studies.

The satisfactory analytical data and all the results presented above suggest that the resulting complexes are of the general composition $K_2[Co(NO)(CN)_4(L)] \cdot H_2O$. Thus, it is reasonable to propose a tetragonally distorted[21] octahedral structure for these complexes having the ligand L in an axial position *trans* to NO^+ and four cyanide ligands at the equatorial positions.

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