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Articles

Synthesis and Characterization of a Series of Tripodal Transition Metal Complexes with the Schiff Base of 2,2′,2″-Triaminoethylamine and 2-Pyridinecarboxaldehyde *N*-Oxide. Crystal Structures of Heptacoordinate Manganese(II) and Cobalt(II) Complexes of a Seven-Coordinate Ligand

Shaohua Gou,* Xiaozeng You, Kaibei Yu,[†] and Jianping Lu[‡]

Coordination Chemistry Institute, Nanjing University, Nanjing 210008, P.R. China

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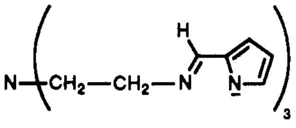
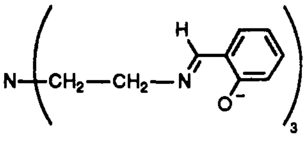
A series of tripodal transition metal complexes with the condensation product of 2,2′,2″-triaminoethylamine (tren) and 2-pyridinecarboxaldehyde *N*-oxide (pyo) as the ligand have been synthesized and spectroscopically characterized. The crystal structures of $[Mn(pyo_3tren)](PF_6)_2{\cdot}C_2H_5OH$ (**1**) and $[Co(pyo_3tren)](PF_6)_2{\cdot}CH_3CN$ (**2**) have been determined. Both **1** and **2** crystallize in the cubic space group $P2_13$ with four formula units. Crystal data: **1**, $a = 15.220(2)$ Å, final $R = 0.045$; **2**, $a = 15.069(2)$ Å, final $R = 0.054$. The X-ray structures of **1** and **2** indicate both complex ions have a heptacoordinate metal center with a coordination polyhedron of the monocapped trigonal antiprism owning C_3 symmetry. $[Ni(pyopyoOHtren)](PF_6)_2{\cdot}H_2O$ (**3**) is a hexacoordinate tripodal complex with three inequivalent arms, which had been confirmed by X-ray diffraction. $[Cu(pyotren)](PF_6)_2$ (**4**), the possible hydrolysis product of $[Cu(pyo_3tren)](PF_6)_2$, is a pentacoordinate copper(II) complex with the configuration of a trigonal bipyramid.

Introduction

Tripodal complexes of transition metals and their derivatives have been widely investigated, since they may serve as candidates for a magnetic resonance imaging agent[1] and models for the unique coordination polyhedra[2-4] in addition to their special chemical, physical, and structural properties. The most common tripodal ligands are composed of the condensation products of tren, $N(CH_2CH_2NH_2)_3$, and some aromatic aldehydes or ketones, which can be classified as two types: (i) Ligands with formally-charged oxygen or nitrogen atoms such as $(pyrol)_3tren$[5] and $(sal)_3tren$[6] form neutral complexes with trivalent metal ions.

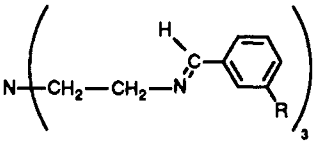


$(pyrol)_3tren$

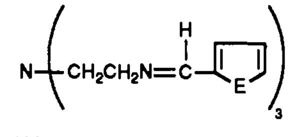


$(sal)_3tren$

(ii) Ligands with neutral nitrogen or sulfur atoms such as $(py)_3tren$[7] and $(thio)_3tren$ or $(fur)_3tren$[8] form complex cations with mono- or divalent metal ions.



$(py)_3tren$ or $(Mepy)_3tren$



$(thio)_3tren$ or $(fur)_3tren$ (E = O, S)

Recently, the ferrocenyl group has also been introduced to this kind of tripodal complexes for magnetic study.[9]

The most thoroughly studied tripodal compounds are the transition metal complexes of $(py)_3tren$ that could be acted as a potential heptacoordinate ligand. As early as the 1960s, the unique action of the N (bridgehead) atom in $[M(py_3tren)]^{2+}$, on both coordination and structure, has attracted attention,[10] because the tertiary amine N atom with a lone pair of electrons may form a bonding or a nonbonding interaction with the metal ion. X-ray crystal structures of the BF_4^- and PF_6^- salts of $[M(py_3tren)]^{2+}$ [10,11] reveal that the potential heptacoordinate $(py)_3tren$ ligand coordinates to the metal through the three imine and the three pyridine

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[†] Chengdu Center of Analysis and Determination, Academia Sinica, Chengdu 610015, P.R. China.

[‡] Section of Physical Chemistry, Yangzhou TV University, Yangzhou 225002, P.R. China.

(1) Smith, P. H.; Raymond, K. N. *Inorg. Chem.* **1985**, *24*, 3469.
(2) Lions, F.; Martin, K. V. *J. Am. Chem. Soc.* **1957**, *79*, 1572.
(3) Fleisher, E. B.; Gebala, A. E.; Tasker, P. A. *J. Am. Chem. Soc.* **1970**, *92*, 6365.
(4) Parks, J. E.; Wagner, B. E.; Holm, R. H. *Inorg. Chem.* **1971**, *10*, 2472.
(5) Sim, P. G.; Sinn, E. *Inorg. Chem.* **1978**, *17*, 1288.
(6) Alcock, N. W.; Cook, D. F.; McKenzie, E. D.; Worthington, J. M. *Inorg. Chem. Acta* **1980**, *38*, 107.
(7) Kichner, R. M.; Mealli, C.; Bailey, M.; Howe, N.; Torre, L. P.; Wilson, L. J.; Andrews, L. C.; Rose, N. J.; Lingafelter, E. C. *Coord. Chem. Rev.* **1987**, *77*, 89.
(8) Alyea, E. C.; Ferguson, G.; Jennings, M.; Li, B.; Xu, Z.; You, X.; Liu, S. *Polyhedron* **1990**, *9*, 2463.
(9) Gou, S.; Xu, Z.; Lu, J.; You, X.; Zhu, D.; Yu, Y. *Acta Chim. Sin.* **1992**, *50*, 1105.
(10) Wilson, L. J.; Rose, N. J. *J. Am. Chem. Soc.* **1968**, *90*, 6041.
(11) Mealli, C.; Lingafelter, L. C. *J. Chem. Soc., Chem. Commun.* **1970**, 885.

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nitrogen atoms, but the distances between the metal atom and the tertial amine N atom are long (>2.79 Å, greater than the sum of the Van der Waals radii).[7] The coordination polyhedra of the above complexes are best described as trigonal antiprisms that are considerably distorted toward a trigonal prism.

To date, although many tripodal metal complexes have been reported, it appears that there is no example of the actual heptacoordinate manganese(II) and cobalt(II) complexes with only one seven-coordinate ligand.[12-14] In this paper, we introduce a new series of tripodal complexes with the condensation product of 2,2′,2″-triaminoethylamine and 2-pyridinecarboxaldehyde *N*-oxide as the ligand and report the crystal structures of the heptacoordinate manganese(II) and cobalt(II) complexes as well as the different coordination cases of related nickel(II) and copper(II) complexes.

Experimental Section

All metal chlorides, potassium hexafluorophosphate, and 2,2′,2″-triaminoethylamine were commercial products of reagent grade and used without further purification. 2-Pyridinecarboxaldehyde *N*-oxide was prepared according to Jerchel's method[15] and confirmed by elemental analysis and IR spectra. UV spectra were obtained employing a Shimadzu 240 instrument. Infrared spectra from 400–4000 cm^{-1} were recorded on a Nicolet 170 SX-FTIR spectrometer, with samples prepared as solid KBr pellets. Magnetic susceptibility was carried out in the solid state at room temperature using a CTP-F82 Faraday magnetometer with $[Ni(en)_3]S_2O_3$ as a calibrant.

Syntheses. An in situ reaction was used to prepare the metal complexes, due to the difficult isolation of the condensed product of tren and pyo. A typical procedure is as follows: 1.107 g (9 mmol) of pyo and 0.438 g (3 mmol) of tren were dissolved in 60 mL of water and filtered. The resulting filtrate was mixed with an aqueous solution of $MCl_2{\cdot}nH_2O$ (3 mmol; M = Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) in 20 mL of water and then stirred at room temperature. After 10 min, a filtered solution of 1.472 g (8 mmol) of KPF_6 in 20 mL of water was added into the above solution; the mixture was kept cool overnight in a refrigerator. The solid hexafluorophosphate salt was precipitated from the solution. The precipitation was filtered and washed with a small amount of cold water and absolute ethanol and dried under vacuum over P_2O_5. Complexes of Mn^{2+}, Ni^{2+}, and Cu^{2+} were prepared by the above method. $[Mn(pyo_3tren)](PF_6)_2{\cdot}H_2O$ (**1a**): brown-red crystals; 32% yield. Anal. Calcd for $MnC_{24}H_{28}F_{12}N_7O_4P_2$: C, 34.95; H, 3.51; N, 11.89. Found: C, 34.40; H, 3.70; N, 11.54. Infrared (cm^{-1}): 3640–2800 (vs, br), 1654 (s), 1605 (m), 1437 (s), 1205 (s), 839 (vs), 558 (s). $[Ni(pyopyoOHtren)](PF_6)_2{\cdot}H_2O$ (**3**): brown red crystals; 61% yield. Anal. Calcd for $NiC_{18}H_{28}F_{12}N_6O_4P_2$: C, 29.16; H, 3.78; N, 11.34. Found: C, 29.82; H, 3.63; N, 11.00. Infrared (cm^{-1}): 3639–2880 (vs, br), 3388 (m), 3296 (m), 1666 (m), 1609 (m), 1445 (m), 1206 (s), 838 (vs), 559 (s). $[Cu(pyotren)](PF_6)_2$ (**4**): blue crystals; 74% yield. Anal. Calcd for $CuC_{12}H_{21}F_{12}N_5OP_2$: C, 23.82; H, 3.47; N, 11.58. Found: C, 24.62; H, 3.33; N, 11.40. Infrared (cm^{-1}): 3377 (s), 3315 (m), 1667 (m), 1608 (m), 1445 (m), 1201 (m), 834 (vs), 559 (s).

By the general procedure, a complex containing Co^{2+} was prepared in a mixture, probably due to the oxidation of Co^{2+} to Co^{3+} in the solution. The related pure divalent cobalt complex was obtained by recrystallizing the initial product in a blending solvent of $CH_3CN–C_2H_5OH$ (1:1). $[Co(pyo_3tren)](PF_6)_2{\cdot}CH_3CN$ (**2**): brown-red crystals; 40% yield. Anal. Calcd for $CoC_{26}H_{30}F_{12}N_8O_3P_2$: C, 36.66; H, 3.53; N, 13.16. Found: C, 37.48; H, 3.96; N, 12.63. Infrared (cm^{-1}): 2002 (sh), 1650 (s), 1438 (s), 1209 (m), 840 (vs), 558 (s).

X-ray Diffraction Studies. For compounds **1** and **2**, a suitable crystal was chosen for data collection. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.710 73 Å) on a Nicolet R3M/E diffractometer, using a continuous θ–2θ scan mode (2θ range: $1° \leqslant 2\theta \leqslant 45°$). Cell content and orientation matrix were obtained from least-squares refinement, applying the setting angle of certain reflections in a θ range (**1**, 22 reflections, $8° \leqslant 2\theta \leqslant 23°$; **2**, 23 reflections, $6° \leqslant 2\theta \leqslant 23°$), measured by the computer-controlled diagonal slit method of centering. All calculations were performed on a ECLIPSE/S140 computer using the SHELXTL software package.[16]

Table I. Crystallographic Data for $[Mn(pyo_3tren)](PF_6)_2{\cdot}C_2H_5OH$

chem formula	$C_{26}H_{33}F_{12}MnN_7O_4P_2$	fw	852
space group	$P2_13$, cubic	ρ_{calcd}, g cm^{-3}	1.61
a, Å	15.220(2)	*V*, Å^3	3525(1)
F(000)	1731.68	μ (Mo Kα), cm^{-1}	5.52
Z	4	*T*, °C	22 ± 1.5
R^a	0.045	$R_w{}^b$	0.041

[a] $R = \sum|F_o - F_c|/\sum(F_o)$. [b] $R_w = [|F_o - F_c|w^{1/2}]/\sum[F_ow^{1/2}]$.

Table II. Positional and Thermal Parameters and Their Esd's for Selected Atoms for $[Mn(pyo_3tren)](PF_6)_2{\cdot}C_2H_5OH$

atom	*x*	*y*	*z*	U,^{a} Å^2
Mn	0.4146(1)	0.4146(1)	0.4146(1)	0.035(1)
P1	0.1516(1)	0.1516(1)	0.1516(1)	0.049(1)
P2	−0.3081(1)	−0.3081(1)	−0.3081(1)	0.044(1)
F1	0.2546(3)	0.1465(4)	0.1574(4)	0.116(2)
F2	0.1596(5)	0.1521(5)	0.0505(3)	0.152(3)
F3	−0.2762(4)	−0.3939(3)	−0.3553(4)	0.116(2)
F4	−0.2607(4)	−0.3382(4)	−0.2219(3)	0.117(2)
N1	0.5088(3)	0.5088(3)	0.5088(3)	0.046(1)
N2	0.5400(3)	0.4409(3)	0.3383(3)	0.043(2)
N3	0.4018(3)	0.3929(3)	0.2122(3)	0.039(1)
O′	−0.0758(8)	−0.0758(8)	−0.0758(8)	0.195(4)
O	0.3698(3)	0.4363(3)	0.2795(2)	0.047(1)
C1	0.5846(4)	0.5399(4)	0.4547(4)	0.054(2)
C2	0.6146(4)	0.4683(5)	0.3934(4)	0.051(2)
C3	0.5538(4)	0.4243(4)	0.2585(4)	0.046(2)
C4	0.4901(4)	0.3906(3)	0.1961(4)	0.039(2)
C5	0.5185(4)	0.3521(4)	0.1174(4)	0.051(2)
C6	0.4608(5)	0.3127(5)	0.0600(4)	0.060(2)
C7	0.3734(4)	0.3118(4)	0.0820(4)	0.056(2)
C8	0.3453(4)	0.3525(4)	0.1576(4)	0.053(2)
C9	−0.1275(9)	−0.1275(9)	−0.1275(9)	0.220(9)
C10	−0.1445(11)	−0.2183(10)	−0.0848(14)	0.060(7)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

$[Mn(pyo_3tren)](PF_6)_2{\cdot}C_2H_5OH$ (1). Brown-red single crystals were developed from the solution of **1a** in a mixed solvent of $CH_3CN–C_2H_5OH$ (1:1). The crystal used had dimensions 0.52 × 0.36 × 0.30 mm. Crystallographic data are summarized in Table I.

A systematic search of a limited hemisphere of reciprocal space revealed intensities with two Laue groups choices. Following complete intensity data collection, a more careful inspection revealed systematic absences that determined space group $P2_13$ on the basis of Laue symmetry. A total of 2658 reflections was collected of which 849 reflections with $I \geqslant 3\sigma(I)$ were considered as observed. Lorentz and polarized correction were applied to the data; no absorption correction was made. A secondary extinction correction was applied. The structure was solved by direct methods. The position of Mn atom was located from an *E*-map. All remaining atoms were located in succeeding difference Fourier synthesis. Hydrogen atoms were defined from the difference Fourier map. Largest shift/esd is 0.078, electron density in final difference map, $\Delta\rho_{max}$ = 0.766, and $\Delta\rho_{min}$ = 0.232 e/Å^3. The weights scheme, $w = [\sigma^2(F_o) + 0.0001F_o^2]^{-1}\,[1 - \exp(-5\sin(\theta/\lambda))^2]$, was used to give maximum weight to intermediate reflections.

$[Co(pyo_3tren)](PF_6)_2{\cdot}CH_3CN$ (2). Brown-red single crystals were also obtained from $CH_3CN–C_2H_5OH$ (1:1). The crystal used had dimensions 0.40 × 0.36 × 0.20 mm. Crystallographic data are summarized in Table IV.

Data were collected under conditions similar to those used for Mn compound. 2560 reflections were collected and averaged to give 804 observed reflections $I \geqslant 3\sigma(I)$. The data was corrected by the same corrections. The structure was solved by direct methods as well. The Co atom and other non-H atoms were located in the same way as in complex **1**. Largest shift/esd is 0.101, $\Delta\rho_{max}$ = 0.950, and $\Delta\rho_{min}$ = −0.659 e/Å^3. The same weighting scheme as the Mn compound was applied to give the final *R* and R_w.

Results and Discussion

Syntheses and Spectral Study. Although the reaction of tren with pyo in water can be easily carried out, the condensation

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(12) Boggess, R. K.; Wiegele, W. D. *J. Chem. Educ.* **1978**, *55*, 156.
(13) Drew, M. G. B. *Prog. Inorg. Chem.* **1977**, *23*, 67.
(14) Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 41.
(15) Jerchel, D.; Heider, J.; Wagner, H. *Justus Liebigs Ann. Chem.* **1958**, *613*, 155.
(16) Sheldrick, G. M. *SHELXTL Users Manual, Revision 4*; Nicolet XRD Corp.: Madison, WI, 1983.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Mn(pyo_3tren)](PF_6)_2{\cdot}C_2H_5OH$[a]

Mn–N1	2.483(8)	Mn–N2	2.270(4)
Mn–O	2.192(3)	P1–F1	1.572(5)
P1–F2	1.544(5)	P2–F3	1.566(5)
P2–F4	1.566(5)	N1–C1	1.494(7)
N2–C2	1.471(7)	N2–C3	1.257(7)
N3–O	1.313(5)	N3–C4	1.366(7)
N3–C8	1.344(8)	O′–C9	1.362(31)
C1–C2	1.506(9)	C3–C4	1.452(8)
C4–C5	1.403(8)	C5–C6	1.378(9)
C6–C7	1.372(10)	C7–C8	1.374(9)
C9–C10	1.549(19)		
N1–Mn–N2	73.0(1)	N1–Mn–O	129.4(1)
N2–Mn–O	75.8(1)	N2–Mn–N2a	111.8(1)
O–Mn–N2a	83.1(1)	N2–Mn–Oa	157.1(2)
O–Mn–Oa	84.0(2)	Mn–N1–C1	108.1(4)
C1–N1–C1a	110.8(3)	Mn–N2–C2	114.0(3)
Mn–N2–C3	126.8(4)	C2–N2–C3	118.6(5)
O–N3–C4	121.2(4)	O–N3–C8	118.3(5)
C4–N3–C8	120.4(5)	Mn–O–N3	122.7(3)
N1–C1–C2	110.2(5)	N2–C2–C1	108.9(5)
N2–C3–C4	126.2(5)	N3–C4–C3	122.1(5)
N3–C4–C5	117.9(5)	C3–C4–C5	120.0(5)
C4–C5–C6	121.8(6)	C5–C6–C7	117.9(6)
C6–C7–C8	120.1(6)	N3–C8–C7	121.7(6)
O′–C9–C10	111.7(11)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Crystallographic Data for $[Co(pyo_3tren)](PF_6)_2{\cdot}CH_3CN$

chem formula	$C_{26}H_{30}CoF_{12}N_8O_3P_2$	fw	851
space group	$P2_13$, cubic	ρ_{calcd}, g cm^{-3}	1.65
a, Å	15.069(2)	V, Å^3	3422(1)
F(000)	1723.65	μ (Mo Kα), cm^{-1}	6.96
Z	4	T, °C	22 ± 1.5
R^a	0.054	$R_w{}^b$	0.050

[a] $R = \sum|F_o - F_c|/\sum(F_o)$. [b] $R_w = [|F_o - F_c|w^{1/2}]/\sum[F_ow^{1/2}]$.

product is difficult to isolate. It has been reported that ferrous salts may serve as reducing agents for deoxygenating *N*-oxides;[17] perhaps this is the reason that we have not obtained the related Fe(II) complex. Carvey et al. pointed out that the majority of the metal complexes of aromatic amine *N*-oxides are decomposed by water,[18] but it is not useful to change solvent in our syntheses.

No useful information about the d–d transition of metal ions is obtained from the electronic spectra of the complex in a solution of acetonitrile. The relevant d–d bands are undetermined except a strong band at 35 714 cm^{-1} attributed to the $\pi \rightarrow \pi^*$ transition of the ligand.[19]

In the IR spectra of complexes **1**–**4**, characteristic ν(C=N) frequencies are all observed in the range 1650–1670 cm^{-1}, and ν(N—O) appears near 1205 cm^{-1}. In comparison with that of the corresponding pyridine *N*-oxides,[20–22] ν(N–O) of the ligand decreases by ca. 25–42 cm^{-1}, indicating the coordinated oxygen atom of the N–O bond. In addition, all complexes show a very strong band at approx. 840 cm^{-1}, assigned to the stretching vibration of P–F bonds in the hexafluorophosphurate anion group. Complex **1a** has a broad water absorption in the region 2800–3640 cm^{-1}, due to the existence of crystalline water.[23] A sharp band at 2002 cm^{-1} is observed in complex **2**, which is assigned to ν(C≡N), illustrating the presence of CH_3CN in this compound. Both complexes **3** and **4** also have bands in the region of 3300–3400 cm^{-1} assigned to ν(N–H), demonstrating the presence of independent amino groups, which indicate that not all three aminos in tren have condensed with the aldehyde. IR absorptions of the crystalline water are found in complex **3** as well.

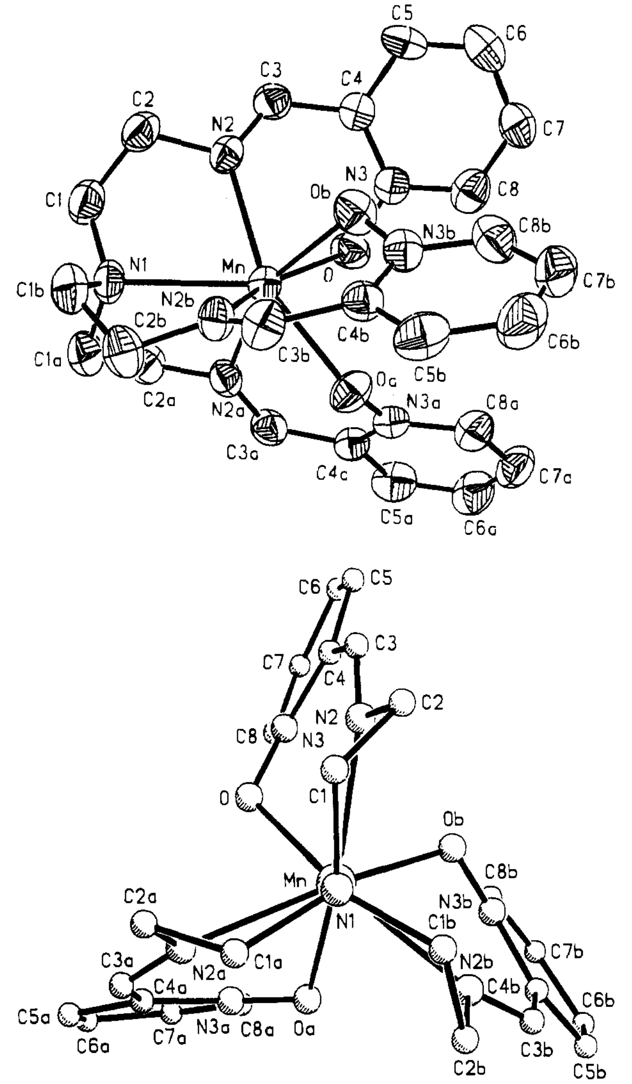

Figure 1. (a) ORTEP drawing of $[Mn(pyo_3tren)]^{2+}$ and (b) a view of the C_3 symmetry along the N1–Mn axis.

Structure Discussion. Both manganese(II) and cobalt(II) compounds have essential the same molecular geometry; the crystallographic data proved that their crystal structures are isostructural. The corresponding views are shown in Figures 1 and 2, respectively. The metal and N1 atoms are on crystallographic C_3 axes, the asymmetric unit being one-third of the complex ion (see Figures 1b and 2b). Results of the atomic coordinates and molecular geometries are presented in Tables II, III, V, and VI.

The coordination polyhedra of Mn and Co atoms are monocapped antitrigonal prisms with a unit of $[MN_4O_3]$, in which the bridging N(1) atom is bonded with the metal atom.[24] Three nitrogen atoms of the C=N bonds and three oxygen atoms of the *N*-oxides form two ideal equilateral triangles between which the metal atom is located. On the top of the N_3 triangle lies the bridging N1 atom. The N_3 and O_3 equilateral triangles, which parallel each other, are mutually staggered by 54.4° for the Mn complex and 60.3° for the Co complexes, respectively. The distortion of staggered angle from the ideal state (60°) results in the different N(2)–O distance of 2.743 and 2.959 Å in the Mn complex, and 2.725 and 2.735 Å in the Co complex. This demonstrates that the structure composed of a N_4O_3 unit here

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(17) Abramovitch, R. A.; Adams, K. A. H. *Can. J. Chem.* **1961**, *39*, 2134.
(18) Garvey, R. G.; Nelson, J. H.; Ragslak, R. O. *Coord. Chem. Rev.* **1968**, *3*, 375.
(19) Ito, M.; Hata, N. *Bull. Chem. Soc. Jpn.* **1955**, *28*, 260.
(20) Kakiuti, Y.; Kida, S.; Quagliao, J. V. *Spectrochim. Acta* **1963**, *19*, 189.
(21) Katritzky, A. R.; Hards, A. R. *J. Chem. Soc.* **1958**, 2195.
(22) Gou, S.; You, X.; Xu, Z.; Yu, K.; Zhou, Z. *Polyhedron* **1990**, *9*, 2981.
(23) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; John Wiley: New York, 1978, p 231.
(24) Gou, S.; Xu, Z.; You, X.; Yu, K. *Chin. Chem. Lett.* **1991**, *2*, 801.

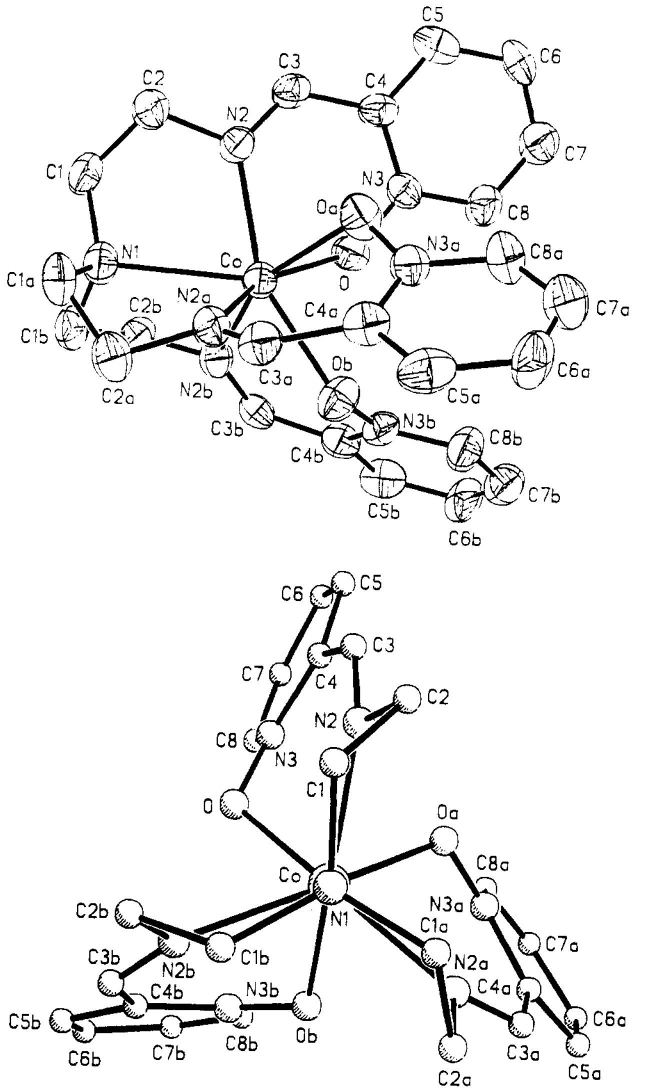

Figure 2. (a) ORTEP drawing of $[Co(pyo_3tren)]^{2+}$ and (b) a view of the C_3 symmetry along the N1–Co axis.

Table V. Positional and Thermal Parameters and Their Esd's for Selected Atoms for $[Co(pyo_3tren)](PF_6)_2{\cdot}CH_3CN$

atom	*x*	*y*	*z*	*U*,[a] Å²
Co	0.3316(1)	0.3316(1)	0.3316(1)	0.032(1)
P1	0.0557(1)	0.0557(1)	0.0557(1)	0.039(1)
P2	0.6008(2)	0.6008(2)	0.6008(2)	0.045(1)
F1	–0.0355(4)	0.0839(4)	0.0125(4)	0.086(2)
F2	0.0971(5)	0.1461(4)	0.0266(5)	0.090(2)
F3	0.6054(5)	0.4961(4)	0.5944(5)	0.105(3)
F4	0.5928(7)	0.7026(4)	0.6021(7)	0.137(4)
N1	0.2380(4)	0.2380(4)	0.2380(4)	0.041(2)
N2	0.3123(4)	0.2104(4)	0.4042(4)	0.036(2)
N3	0.3528(4)	0.3526(4)	0.5322(4)	0.035(2)
N4	–0.1944(24)	–0.1944(24)	–0.1944(24)	0.369(29)
O	0.3068(4)	0.3818(3)	0.4637(3)	0.043(2)
C1	0.2121(5)	0.1598(5)	0.2919(5)	0.045(3)
C2	0.2885(6)	0.1323(6)	0.3510(5)	0.042(3)
C3	0.3292(5)	0.1966(5)	0.4852(5)	0.036(2)
C4	0.3596(5)	0.2637(5)	0.5495(5)	0.038(3)
C5	0.3992(6)	0.2374(6)	0.6290(6)	0.049(3)
C6	0.4354(6)	0.3000(7)	0.6872(5)	0.052(3)
C7	0.4303(6)	0.3858(6)	0.6634(6)	0.050(3)
C8	0.3899(6)	0.4122(5)	0.5881(5)	0.047(3)
C9	–0.1500(20)	–0.1500(20)	–0.1500(20)	0.215(17)
C10	–0.0930(16)	–0.0930(16)	–0.0930(16)	0.359(60)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[Co(pyo_3tren)](PF_6)_2{\cdot}CH_3CN$[a]

Co–N1	2.445(11)	Co–N2	2.149(6)
Co–O	2.161(5)	P1–F1	1.579(6)
P1–F2	1.561(6)	P2–F3	1.582(7)
P2–F4	1.539(7)	N1–C1	1.483(9)
N2–C2	1.468(10)	N2–C3	1.264(10)
N3–O	1.319(8)	N3–C4	1.369(10)
N3–C8	1.352(10)	N4–C9	1.158(81)
C1–C2	1.514(12)	C3–C4	1.473(11)
C4–C5	1.397(12)	C5–C6	1.399(13)
C6–C7	1.343(13)	C7–C8	1.348(12)
C9–C10	1.488(66)		
N1–Co–N2	74.0(2)	N1–Co–O	129.3(2)
N2–Co–O	78.8(2)	N2–Co–N2a	112.7(1)
O–Co–N2a	156.6(2)	N2–Co–Oa	78.4(2)
O–Co–Oa	84.1(2)	Co–N1–C1	107.1(5)
C1–N1–C1a	111.7(5)	Co–N2–C2	115.9(5)
Co–N2–C3	127.2(5)	C2–N2–C3	116.4(6)
O–N3–C4	121.0(6)	O–N3–C8	118.9(6)
C4–N3–C8	120.1(6)	Co–O–N3	120.9(4)
N1–C1–C2	109.8(7)	N2–C2–C1	106.7(7)
N2–C3–C4	125.8(7)	N3–C4–C3	121.6(7)
N3–C4–C5	118.2(7)	C3–C4–C5	120.2(7)
C4–C5–C6	120.9(8)	C5–C6–C7	117.3(8)
C6–C7–C8	122.3(8)	N3–C8–C7	121.0(7)
N4–C9–C10	180.0(1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Selected Distances of Metal–N (bridging atom)

compd	M–N, Å	metal	ref
$[Mn(py_3tren)](BF_4)_2$	2.794(2)	Mn(II)	7
$[Mn(pyo_3tren)](PF_6)_2{\cdot}C_2H_5OH$	2.483(1)	Mn(II)	this paper
$[Mn(sal_3tren)]$	3.229(6)	Mn(III)	6
$[Co(py_3tren)](BF_4)_2$	2.870(2)	Co(II)	7
$[Co(pyo_3tren)](PF_4)_2{\cdot}CH_3CN$	2.445(11)	Co(II)	this paper

has a distortion from one ideal trigonal antiprism. The M–N1 bond is significantly longer than that of M–N2 [**1**, 2.270(4) Å; **2**, 2.149(1) Å], but it is much stronger than the literature reported. Related atomic distances between the metal and the bridging N1 atom in the corresponding complexes are listed in Table VII for comparison.

It has been reported that $[Mn(py_3tren)]^{2+}$ [7] is the most distorted from a regular octahedral coordination polyhedron; the Mn to N1 distance is slightly less than the sum of the van der Waals radii and is better described as six-coordinate. In comparison, complex **1** has a short Mn–N1 bond very much less than the corresponding sum of the van der Waals radii, forming a stronger coordination bond. $[Co(py_3tren)](BF_4)^{2+}$, which has a lone pair of electrons on N(1) "appearing to float on the Van der Waals surface of the metal ion", can only be considered to be potentially heptacoordinate. However, in complex **2**, the strong coordination bond of Co–N1 leads to the actual heptacoordinate configuration of the cobalt atom. This is because the pyridine *N*-oxide groups lead to smaller steric crowding.

McKenzie et al.[6,25,26] reported a series of tripodal trivalent metal complexes in the form of $[M(sal_3tren)]$, where sal_3tren moieties are the condensized product of 5-chlorosalcylaldehyde and tren and M^{3+} are Fe, Cr, and Mn. The X-ray crystal data demonstrated that the three complexes mentioned above are isostructural, with the $[MN_3O_3]$ octahedra being close to an ideal one. Although the metal and bridging N(1) atoms are on the C_3 axes, they are nonbonded. The difference of the coordination ability of N(1) atom between salicylaldiminates and pyridine *N*-oxides results from their unique ligand geometries of the two kinds of complexes. The ligand moiety in complexes **1** and **2** causes a greater spreading of the three N2 atoms and less compression than those reported for $[M(sal_3tren)]$.

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(25) Cook, D. F.; Cummings, D.; McKenzie, E. D. *J. Chem. Soc., Dalton Trans.* **1976**, 1369.

(26) Bailey, N. A.; Cook, D. F.; Cummings, D.; McKenzie, E. D. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 51.

The crystal structure of [Ni(pyopyoOHtren)]$(PF_6)_2 \cdot H_2O$ has been reported earlier.[27] The nickel(II) atom in this complex is in a distorted octahedral environment of a tripodal ligand with three inequivalent arms in which the bridging N atom has a distance of 2.065(4) Å from the metal atom forming the normal coordination N–Ni bond. It is of great interest that a stable carbinolamine intermediate is found existing in one of three arms through the formation of hydrogen bond with crystalline water. Complex **3**, therefore, turns out to be the first example with a hexacoordinated configuration composed of different tripodal arms.

It has been reported that, compared with the other $[M(py_3tren)]^{2+}$ complexes,[28] $[Cu(py_3tren)]^{2+}$ is unstable with respect to hydrolysis, which generates $[Cu(pytren)]^{2+}$ by losing two aromatic aldehydes. The solvent used in our reaction is water and the product is $[Cu(pyotren)]^{2+}$ instead of $[Cu(pyo_3tren)]^{2+}$, presumably due to hydrolysis. This is confirmed by microanalyses and IR spectra. This property indicates that the copper ion in both $[Cu(pyotren)]^{2+}$ and $[Cu(pytren)]^{2+}$ shares common natures in coordination ability with these two tripodal ligands. The configuration of complex **4** may be a distorted trigonal bipyramidal coordination polyhedron comprised of four nitrogen and one oxygen atoms of pyotren ligand, similar to those found in $[M(tren)(NCS)]^{2+}$ (M^{2+} = Cu, Zn),[29,30] $[M(Me_6tren)X]^+$ [M^{2+} = Cu, Zn; Me_6tren = $N(CH_2CH_2N(CH_3)_2)_3$],[31,32] and $[Cu(pytren)]^{2+}$ [7] where a tren moiety is acting as a tripodal ligand with "a unique tertiary nitrogen atom occupying the axial site and the remaining nitrogen atoms the three equatorial sites". But no structural data is available here for comparison.

Table VIII. Solid Magnetic Data for Complexes **1–4**

compd	temp, K	$10^{-6}\chi_{M(corr)}$,[a] cgsu	μ_{eff}, μ_B
1a	283	15,887	6.00
2	283	12,413	5.30
3	283	4,232	3.10
4	283	1,577	1.89

[a] Corrected molar susceptibility. Diamagnetic: **1a**, -390×10^{-6} cgsu; **2**, -397×10^{-6} cgsu; **3**, -363×10^{-6} cgsu; **4**, -285×10^{-6} cgsu.

Magnetic Properties. Magnetic susceptibility data are listed in Table VIII. Values of μ_{eff} in μ_B have been calculated using the equation $\mu_{eff}(\mu_B) = 2.828[\chi_{M(cor)}T]^{1/2}$. The molar diamagnetic corrections used in determining the $\chi_{M(cor)}$ values have been calculated from Pascal's constants.[33] It is evident from the μ_{eff} data that both complexes **1** and **2** are in high-spin states like other tripodal Mn and Co complexes.[34]

Magnetic moment data for complexes **3** and **4** are in the normal range for divalent nickel and copper compounds. Due to the resemblance of molecular structures, both **3** and **4** have μ_{eff} values very close to those of their corresponding complexes, $[Ni(py_3tren)](PF_6)_2$ with a μ_{eff} value of 3.05 μ_B at 300 K and $[Cu(pytren)](PF_6)_2$ with a value of 1.84 μ_B at 297 K.[7]

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Supplementary Material Available: Figures showing the crystal structure and unit cell, text describing the experimental procedures of the structure determination, and tables giving crystal data and details of the structure determination, atom coordinates, bond lengths and bond angles, anisotropic thermal parameters, hydrogen atom locations, and least-squares planes for **1** and **2** (35 pages). Ordering information is given on any current masthead page.

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(27) Gou, S.; You, X.; Xu, Z.; Liu, S.; Lin, C. *Acta Crystallogr., Sect. C* **1991**, *47*, 708.

(28) Lingafelter, E. C.; Andrews, L. C.; Kichner, R. M.; Rose, N. J.; Wilson, L. J. *Coord. Chem. Rev.* **1972**, *8*, 55.

(29) Jain, P. C.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1967**, *89*, 6131.

(30) Andreetti, G. D.; Jain, P. C.; Lingafelter, E. C. *J. Am. Chem. Soc.* **1969**, *91*, 4112.

(31) Divaira, M.; Orioli, P. L. *Inorg. Chem.* **1967**, *6*, 955.

(32) Divaira, M.; Orioli, P. L. *Acta Crystallogr., Sect. B* **1968**, *24*, 595.

(33) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986; p 3.

(34) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*, Pergamon Press: Oxford, England, 1984; p 1315.