Inorg. Chem. **1999,** *38,* 5457−5460

Trinucleating Bipyridyl Ligands; Synthesis and Structure of Cobalt-Benzoquinone Complex of Cyclotriphosphazenes Bearing Dioxybipyridine Groups

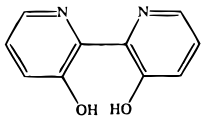
Ok-Sang Jung,*,† Yong Tae Kim,† Young-A Lee,† Yun Ju Kim,† and Hee K. Chae‡

Materials Chemistry Research Center, Korea Institute of
Science and Technology, Seoul 136-791, Korea, and
Department of Chemistry, Hankuk University of
Foreign Studies, Yongin 449-791, Korea

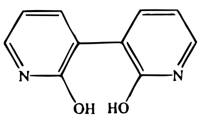
Received February 23, 1999

Introduction

Various polypyridyl ligands that can bridge two or more remote metal centers have been used to construct elaborate molecular structures. Current applications of such polynuclear complexes span the wide range of mixed valence species, photoinduced electron or energy transfer, magnetic exchange between paramagnetic centers, and supramolecular structures.[1−3] Ligands that can bind three or more metal ions are relatively rare in contrast to the vast majority of dinucleating ligands. In this context, there have been constant attempts to explore the metal complexes of substituted cyclotriphosphazenes containing nitrogen donor side groups.[4−9] Their structural and physicochemical properties have been found to be delicately dependent upon the nature of the ligands. Some cyclotriphosphazenes containing bipyridine groups may offer wider opportunities for trigonal array due to the ease of introduction of desirable functional groups. We now describe new interesting trinucleating ligands prepared from the reaction of hexachlorocyclotriphosphazene with 3,3′-dihydroxy-2,2′-bipyridine (3,2-HObpy) or 2,2′-dihydroxy-3,3′-bipyridine (2,3-HObpy).[10,11] The new tris(diimine) ligands have been applied to synthesize Co(N−N)(bq)$_2$ (bq = *o*-benzoquinone) which is susceptible to the N−N ligand.[12−15]



3,2-HObpy



2,3-HObpy

Experimental Section

Chemicals and Measurements. Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) and 3,5-dbbq (3,5-di-*tert*-butyl-*o*-benzoquinone) were purchased from Aldrich, and $Co_2(CO)_8$ was from Strem. 3,2-HObpy,[10] 2,3-HObpy,[11] and 3,6-dbbq (3,6-di-*tert*-butyl-*o*-benzoquinone)[16] were prepared by the respective literature methods. Chemical analyses were carried out by the Advanced Analysis Center at KIST. IR spectra were recorded on a Perkin-Elmer 16F PC model FTIR spectrometer as KBr pellets. NMR spectra were measured on a Varian Gemini 300 NMR spectrometer operating at 300.00 MHz (^{1}H), 75.48 MHz (^{13}C), and 121.44 MHz (^{31}P) in pulse mode with Fourier transform. The chemical shifts were relative to internal Me_4Si (^{1}H and ^{13}C) and external $(C_6H_5O)_3PO$ (^{31}P)[17] for the indicated nuclei. Temperature-dependent magnetic measurements were made using a Quantum Design MPMS-5 SQUID magnetometer at a field of strength 10 kG. EPR spectra were recorded on a Bruker Quantum Design MPMS 5 and referenced to DPPH as the *g* value standard. Electronic spectra were recorded on a Perkin-Elmer UV/VIS/NIR Spectrometer Lambda 19. Thermal analysis was performed on a Stanton Red Croft TG 100 with a scanning rate of 20 °C/min when heating.

N_3P_3(3,2-Obpy)$_3$. $N_3P_3Cl_6$ (1.74 g, 5.0 mmol) and triethylamine (5.06 g, 50 mmol) were combined in 100 mL of dried tetrahydrofuran. The mixture was stirred for 5 min at room temperature, and 3,2-HObpy (3.01 g, 16.0 mmol) was added. The reaction solution was refluxed for 3 days. The white precipitate was washed with water to get rid of triethylamine hydrochloride, and then dried. Recrystallization from a mixture of dichloromethane and toluene (1:1) gave colorless crystals suitable for X-ray crystallography: mp 290 °C dec (solvate dichloromethane and toluene molecules were evaporated at a wide range of 40−180 °C). Yield 75.2%. Anal. Found (Calcd for $C_{30}H_{18}N_9O_6P_3 \cdot CH_2Cl_2 \cdot C_6H_5CH_3$): C, 52.50 (52.43); H, 3.27 (3.24); N,14.53 (14.48). IR (KBr, cm^{-1}): ν(P=N), 1218, 1164. ^{1}H NMR (CDCl, ppm): 8.77 (1H, d, 4.4 Hz), 7.70 (1H, d, 8.0 Hz), 7.48 (1H, dd, 4.8 Hz, 3.6 Hz), 7.10−7.30 ($C_6\mathit{H}_5CH_3$), 5.29 (CH_2Cl_2), 2.35 ($C_6H_5\mathit{CH}_3$). ^{13}C NMR (CDCl$_3$, ppm): 148.49, 145.99, 145.59, 129.65, 125.59; CH_2Cl_2 (53.47); $\mathit{C}_6\mathit{H}_5CH_3$ (137.88, 129.04, 128.22, 125.29, 21.34). ^{31}P NMR (CDCl$_3$, ppm): 49.6. ^{31}P NMR (Me$_2$SO-d_6, ppm): 48.0.

N_3P_3(2,3-Obpy)$_3$. $N_3P_3Cl_6$ (1.74 g, 5.0 mmol) and triethylamine (5.06 g, 50 mmol) were combined in 100 mL of dried pyridine. The mixture was stirred for 5 min at room temperature, and 2,3-HObpy (3.01 g, 16.0 mmol) was added. The reaction solution was refluxed for 3 days. The white solids obtained were washed with water, and then dried. Recrystallization from dichloromethane gave white powder: mp 278 °C dec. Yield 92.2%. Anal. Found (Calcd for $C_{10}H_6N_3O_2P$): C, 51.28 (51.96); H, 2.59 (2.62); N, 17.96 (18.18). IR (KBr, cm^{-1}): ν(P=N), 1208, 1172. ^{1}H NMR (Me$_2$SO-d_6, ppm): 8.47 (1H, d, 4.0 Hz), 8.33

---

* To whom correspondence should be addressed. E-mail: oksjung@kistmail.kist.re.kr.

† Korea Institute of Science and Technology.

‡ Hankuk University of Foreign Studies.

(1) Catalano, V. J.; Larson, W. E.; Olmstead, M. M.; Gray, H. B. *Inorg. Chem.* **1994**, *33*, 4502.

(2) Baba, A. I.; Ensley, H. E.; Schmehl, R. H. *Inorg. Chem.* **1995**, *34*, 1198.

(3) Amoroso, A. J.; Thomson, A. M. W. C.; Maher, J. P.; McCleverty, J. A.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 4828.

(4) Thomas, K. R. J.; Chandrasekhar, V.; Scott, S. R.; Hallford, R.; Cordes, A. W. *J. Chem. Soc., Dalton Trans.* **1993**, 2589.

(5) Chandrasekaran, A.; Krishnamurthy, S. S.; Nethaji, M. *Inorg. Chem.* **1993**, *32*, 6102.

(6) Difenbach, U.; Allcock, H. R. *Inorg. Chem.* **1994**, *33*, 4562.

(7) Carriedo, G. A.; Elipe, P. G.; Alonso, F. J. G.; Fernandes-Catuxo, L.; Diaz, M. R.; Granda, S. G. *J. Organomet. Chem.* **1995**, *498*, 207.

(8) Jung, O.-S.; Park, S. H.; Lee, Y.-A.; Cho, Y.; Kim, K. M.; Lee, S.; Chae, H. K.; Sohn, Y. S. *Inorg. Chem.* **1996**, *35*, 6899.

(9) Jung, O.-S.; Kim, Y. T.; Lee, H.; Kim, K. M.; Chae, H. K.; Sohn, Y. S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2125.

(10) Msahiko, I.; Hiroki, O.; Koichi, S. Nobue, H.; Masaji, O. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 80.

(11) Eckehard, V. *Liebigs Ann. Chem.* **1992**, 953.

(12) Jung, O.-S.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 1127.

(13) Jung, O.-S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 2227.

(14) Jung, O.-S.; Jo, D. H.; Lee, Y.-A.; Conklin, B. J.; Pierpont, C. G. *Inorg. Chem.* **1997**, *36*, 19.

(15) Jung, O.-S.; Jo, D. H.; Lee, Y.-A.; Sohn, Y. S.; Pierpont, C. G. *Inorg. Chem.* **1998**, *37*, 5875.

(16) Belostotskaya, I. S.; Komissarova, N. L.; Dzhuaryan, E. V.; Ershov, V. V. *Izv. Akad. Nauk SSSR* **1972**, 1594. The 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-dbbq) ligand has been shown to be capable of chelating metals as unreduced 3,6-di-*tert*-butyl-*o*-benzoquinone (3,6-dbbq), as partially reduced 3,6-di-*tert*-butyl-*o*-semiquinone (3,6-dbsq) or as fully reduced 3,6-di-*tert*-butyl-catecholate (3,6-dbcat). The term "3,6-dbbq" is used for ligands derived from 3,6-di-*tert*-butyl-*o*-benzoquinone, irrespective of its oxidation state, i.e., 3,6-dbbq, 3,6-dbsq, and 3,6-dbcat. See refs 12−15 and references therein for details.

(17) δ(^{31}P, $(C_6H_5O)_3PO$ = −18 ppm relative to H_3PO_4; Mason, J., Ed. *Multinuclear NMR*, 3rd ed.; Plenum Press: New York 1987, p 375.

10.1021/ic990215d CCC: $18.00

Table 1. Crystallographic Data for $N_3P_3(3,2\text{-}Obpy)_3 \cdot CH_2Cl_2 \cdot C_6H_5CH_3$

formula	$C_{30}H_{18}N_9O_6P_3 \cdot CH_2Cl_2 \cdot C_6H_5CH_3$
fw	870.50
space group	C_2/c
a, Å	21.982(3)
b, Å	18.921(3)
c, Å	10.438(2)
β, deg	106.56(1)
V, Å^3	4162(1)
Z	8
d_{cal}, g cm^{-3}	1.389
absorption coeff, mm^{-1}	0.328
final R indices $\{I > 2\sigma(I)\}$	$R1^a = 0.0777$ $wR2^b = 0.2209$

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR_2 = \sum w(F_o^2 - F_c^2)^2/\sum wF_o^4)^{1/2}$, where $w = 1/\{\sigma^2F_o^2 + (aP)^2 + bP\}$, $P = \{\text{Max}(F_o^2,\text{o}) + 2F_c^2\}/3$.

(1H, d, 6.0 Hz), 7.60 (1H, dd, 4.8 Hz, 2.6 Hz). ^{13}C NMR ($Me_2SO\text{-}d_6$, ppm): 151.50, 148.60, 139.95, 122.70, 120.13. ^{31}P NMR ($Me_2SO\text{-}d_6$, ppm): 45.9.

[N_3P_3(3,2-Obpy)$_3${Co(3,6-dbbq)$_2$}$_3$]. $Co_2(CO)_8$ (171 mg, 0.50 mmol) and N_3P_3(3,2-Obpy)$_3$ (228 mg, 0.33 mmol) were combined in 30 mL of toluene. The mixture was stirred for 5 min, and 3,6-dbbq (440 mg, 2.0 mmol) in 30 mL of toluene was added. The mixture was stirred under dinitrogen atmosphere for 2 h at room temperature. A dark blue solid was obtained in 94% yield. The product was purified in a mixture of toluene and hexane to afford dark blue microcrystals. mp 184−188 °C dec. Anal. Found (Calcd for $C_{38}H_{46}N_3O_6PCo$): C, 62.40 (62.55); H, 6.32 (6.35); N, 5.63 (5.76). IR (KBr, cm^{-1}): 4234 (br, m), 2952 (s), 1830 (m), 1546 (m), 1461 (s), 1440 (s), 1284 (m), 1216 (s, ν(P=N)), 1172 (s, ν(P=N)), 1102 (s), 984 (m), 954 (s), 906 (s), 813 (m), 782 (w), 726 (w), 654 (w), 616 (w), 538 (w).

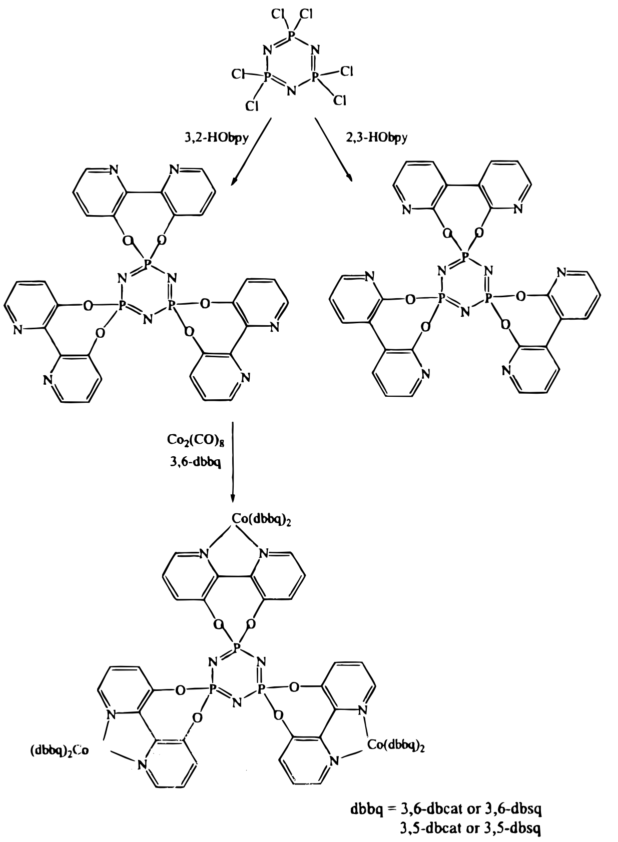
[N_3P_3(3,2-Obpy)$_3${Co(3,5-dbbq)$_2$}$_3$]. $Co_2(CO)_8$ (171 mg, 0.50 mmol) and N_3P_3(3,2-Obpy)$_3$ (228 mg, 0.33 mmol) were combined in 30 mL of toluene. The mixture was stirred for 5 min, and 3,5-dbbq (440 mg, 2.0 mmol) in 30 mL of toluene was added. The mixture was stirred under dinitrogen atmosphere for 2 h at room temperature. The blue solid was obtained in 84% yield. mp 170−172 °C dec. Anal. Found (Calcd for $C_{38}H_{46}N_3O_6PCo$): C, 62.10 (62.55); H, 6.42 (6.35); N, 5.66 (5.76). IR (KBr, cm^{-1}): 2958 (s), 1730 (m), 1640 (w),1584 (m), 1455 (s), 1442 (s, 1440 (s), 1284 (m), 1218 (s, ν(P=N)), 1170 (s, ν(P=N)), 1104 (s), 982 (m), 906 (m), 820 (m), 803 (m), 742 (w), 616 (w), 542 (w).

X-ray Crystallography. For $N_3P_3(3,2\text{-}Obpy)_3 \cdot CH_2Cl_2 \cdot C_6H_5CH_3$, all the crystallographic data were obtained on an Enraf-Nonius CAD 4 automatic diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\alpha_1) = 0.70930$ Å, $\lambda(K\alpha_2) = 0.71359$ Å) at an ambient temperature of 23(2) °C. Preliminary diffractometric investigation indicated a monoclinic system. Accurate cell dimensions were obtained from the setting angles of 25 well-centered reflections by using a least-squares procedure. During the data collection, three standard reflections monitored after every hour did not reveal any systematic variation in intensity. The structure was solved by a direct method, followed by successive difference Fourier synthesis. The nonhydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The solvate dichloromethane molecule was disordered. All calculations were carried out on a personal computer with use of SHELXS 86 or SHELXL 93.[18] Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1. Atomic positions and equivalent isotropic thermal parameters are reported in the Supporting Information.

Results and Discussion

N_3P_3(Obpy)$_3$. The reaction of hexachlorocyclotriphophazene with 3,2-HObpy affords a new cyclotriphosphazene, N_3P_3(Obpy)$_3$.

Scheme 1



The single ^{31}P NMR signal corresponds to the fully substituted cyclotriphosphazene, and its chemical shift (49.6 ppm ($CDCl_3$); 48.0 ppm ($Me_2SO\text{-}d_6$) suggests the P(OR)$_2$ center in cyclotriphosphazene. Among the three possible bonding fashions (geminal, nongeminal, or bridged), only a geminal product was obtained in high yield (Scheme 1). The spirosubstitution at the phosphorus atom seems to be induced by the favorable seven-membered ring at phosphorus.[19] No side products were detected in the reaction. However, when the reaction mixture was refluxed for only 1 day, the bis-substituted product was isolated as a major product. This implies that the present substitution is not a concerted reaction. Another analogue, N_3P_3(2,3-Obpy)$_3$, prepared from the reaction of $N_3P_3Cl_6$ with 2,3-HObpy, was confirmed by elemental analysis and ^{1}H, ^{13}C, and ^{31}P NMR spectra. The ^{31}P chemical shift (45.9 ppm, $Me_2SO\text{-}d_6$) of N_3P_3(2,3-Obpy)$_3$ shifts to high field relative to that (48.0 ppm) of N_3P_3(3,2-Obpy)$_3$. Both compounds are stable up to 278 °C (dec) in contrast to N_3P_3 (2- or 4-OPy)$_6$ (OPy = pyridinoxy) that polymerizes below 200 °C.[20] Such an outstanding difference may be attributed to the chelation effect of the present compounds, suggesting that the ring strain free seven-membered ring obstructs the initiation of the N_3P_3 ring-opening polymerization. Both compounds are air-stable solids and are soluble in polar organic solvents such as dimethyl sulfoxide and dimethylformamide, but are insoluble in water. Interestingly, N_3P_3(3,2-Obpy)$_3$ was soluble in chloroform whereas N_3P_3(2,3-Obpy)$_3$ was insoluble in the solvent.

The X-ray crystal structure of N_3P_3(3,2-Obpy)$_3$ is depicted in Figure 1, and selected bond lengths and bond angles for the asymmetric unit are listed in Table 2. The six-membered ring

---

[18] Sheldrick, G. M. SHELXS-86: A Program for Structure Determination; University of Göttingen, Germany, 1986. Sheldrick, G. M. SHELXL-93: A Program for Structure Refinement; University of Göttingen, Germany, 1993.

[19] Hans, J.; Day, R. O.; Howe, L.; Holmes, R. R. *Inorg. Chem.* **1992**, *31*, 1279.

[20] Cho, Y.; Baik, H. G.; Sohn, Y. S. *Macromolecules* **1999**, *32*, 2167.

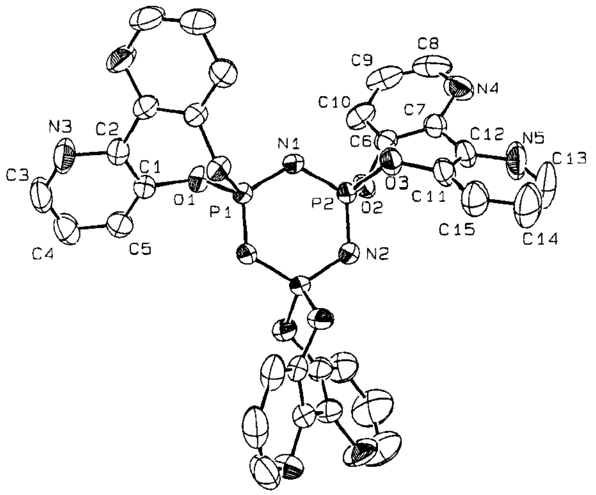


Figure 1. ORTEP view of $N_3P_3(3,2\text{-}Obpy)_3{\cdot}CH_2Cl_2{\cdot}C_6H_5CH_3$. Hydrogen atoms and solvate molecules are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of $N_3P_3(3,2\text{-}Obpy)_3{\cdot}CH_2Cl_2{\cdot}C_6H_5CH_3$

P(1)−O(1)	1.581(4)	P(2)−O(2)	1.583(4)
P(2)−O(3)	1.585(4)	P(1)−N(1)	1.562(4)
P(2)−N(1)	1.575(4)	P(2)−N(2)	1.572(3)
C(1)−O(1)	1.410(6)	C(6)−O(2)	1.398(6)
C(11)−O(3)	1.400(6)		
O(1)−P(1)−O(1)′	103.0(3)	O(1)−P(1)−N(1)′	112.5(2)
O(1)−P(1)−N(1)	105.2(2)	O(1)′−P(1)−N(1)′	105.2(2)
O(1)′−P(1)−N(1)	112.5(2)	N(1)′−P(1)−N(1)	117.8(3)
N(1)−P(2)−N(2)	117.9(2)	N(1)−P(1)−O(2)	112.5(2)
N(2)−P(1)−O(2)	104.8(2)	N(1)−P(1)−O(3)	106.0(2)
N(2)−P(1)−O(3)	112.2(2)	O(2)−P(1)−O(3)	102.3(2)

of N_3P_3 approximates a plane, and the P−N distance, P−N−P angles, and N−P−N angles are very close to those usually encountered in the known cyclotriphosphazenes. The 3,2-Obpy unit is chelated to phosphorus via a spiro type, and thus the local geometry of the phosphorus atom is tetrahedral. The resulting seven-membered exocyclic ring at phosphorus has virtually no effect in widening the angles of O−P−O (103.3(3)°, 102.3(2)°). This is attributed to the marked twisting of the seven-membered ring, i.e., the boat conformation in the solid state. The angles of twist between pyridyl groups in each bipyridyl unit are 41.2(2), 37.7(3), and 37.7(3)° that are essential to sustain the reasonable seven-membered aryldioxyphosphole ring. The three bipyridyl units are arranged in the form of a propeller. The overall structure is very similar to that of tris(2,2′-dioxybiphenyl)cyclotriphosphazene.[21]

$[N_3P_3(3,2\text{-}Obpy)_3\{Co(3,6\text{-}dbbq)_2\}_3]$ and $[N_3P_3(3,2\text{-}Obpy)_3\{Co(3,5\text{-}dbbq)_2\}_3]$. The intramolecular electron transfer between the cobalt ion and quinone ligand for a series of general form Co(N−N)(dbbq)$_2$ has been found to be dependent upon the donor strength of the diimine N−N coligands. That is, the electron transfer could be controlled by the chelate-ring size, the substituent effects, and the conformational change.[12−15] The present compound, $N_3P_3(3,2\text{-}Obpy)_3$, was applied to the Co system as a N−N ligand. The reaction of $Co_2(CO)_8$ with dbbq in the presence of $N_3P_3(3,2\text{-}Obpy)_3$ in toluene affords trinucleating complexes $[N_3P_3(3,2\text{-}Obpy)_3\{Co(dbbq)_2\}_3]$ (Scheme 1). However, the $N_3P_3(2,3\text{-}Obpy)_3$ analogue was not obtained. This is not surprising considering the nitrogen donor atoms of $N_3P_3(2,3\text{-}Obpy)_3$ and bulky *tert*-butyl group of dbbq. The coordination chemistry of $N_3P_3(2,3\text{-}Obpy)_3$ is underway. The analytical and spectroscopic data of $[N_3P_3(3,2\text{-}Obpy)_3\{Co(dbbq)_2\}_3]$ are in accord with the skeletal structure shown in Scheme 1. The infrared spectra (5000−2500 cm^{-1}) shown in Figure 2 disclose the charge distribution of the complexes. For $[N_3P_3(3,2\text{-}Obpy)_3\{Co(dbbq)_2\}_3]$, the broad band centered at 4234 cm^{-1} implies the presence of the $[N_3P_3(3,2\text{-}Obpy)_3\{Co^{III}(3,6\text{-}dbsq)(3,6\text{-}dbcat)\}_3]$ (3,6-dbsq = 3,6-di-*tert*-butylsemiquinone; 3,6-dbcat = 3,6-di-*tert*-butylcatecholate) redox isomer.[12−16] The broad band assigned as 3,6-dbcat to the cobalt(III) charge transfer is less intense and shifts to higher energy than that (3774 cm^{-1}) of Co(bpy)(3,6-dbbq)$_2$.[13] This is our rational control of the Co^{III}/Co^{II} equilibrium induced by the skew conformation[22] of the present bipyridyl unit. For $[N_3P_3(3,2\text{-}Obpy)_3\{Co(3,5\text{-}dbbq)_2\}_3]$, the band around 4000 cm^{-1} was not apparent, indicating that the complex predominantly exists as $[N_3P_3(3,2\text{-}Obpy)_3\{Co^{II}(3,5\text{-}dbsq)_2\}_3]$ at room temperature. Such a fact suggests that the Co(III)/Co(II) transition temperature (T_c) of the 3,5-dbbq complex is much lower than that of the 3,6-dbbq analogue. A band around 3500 cm^{-1} appears due to moisture in the KBr matrix. For $[N_3P_3(3,2\text{-}Obpy)_3\{Co(3,5\text{-}dbbq)_2\}_3]$, the equilibrium was monitored by magnetic measurements on the solid sample over the temperature range from 10 to 400 K (Figure 3). Around 10 K, the cobalt complex is in the low spin $[N_3P_3(3,2\text{-}Obpy)_3\{Co^{III}(3,6\text{-}dbsq)(3,6\text{-}dbcat)\}_3]$ form with $S = {}^1/_2 \times 3$ (per trimer) magnetic moment due to the radical semiquinone ligand (5.1 μB).[15] As the temperature is increased, a shift to the high-spin $[N_3P_3(3,2\text{-}Obpy)_3\{Co^{II}(3,6\text{-}dbsq)_2\}_3]$ redox isomer is observed. In the Co^{II} form, each cobalt unit

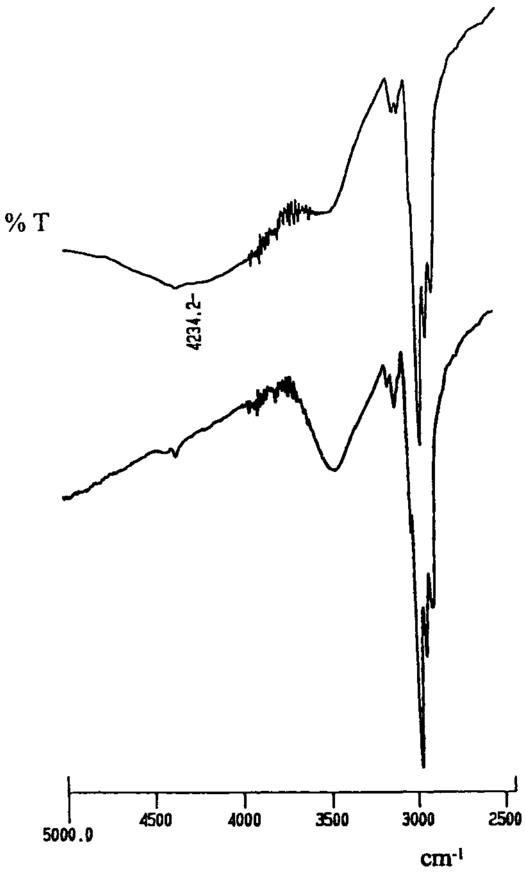


Figure 2. IR spectra of $[N_3P_3(3,2\text{-}Obpy)_3\{Co(3,6\text{-}dbbq)_2\}_3]$ (top) and $[N_3P_3(3,2\text{-}Obpy)_3\{Co(3,5\text{-}dbbq)_2\}_3]$ (bottom) in the range from 5000 to 2500 cm^{-1} showing the presence and absence of a broad band at 4234 cm^{-1}, respectively.

---

[21] Allcock, H. R.; Stein, M. T.; Stanko, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3173.

[22] Gourdon, A. *New J. Chem.* **1992**, *16*, 953.

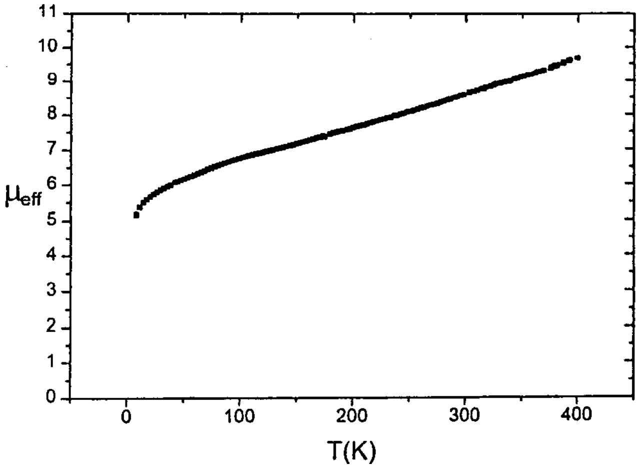


Figure 3. Changes in the magnetic moment of $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,6\text{-dbbq})_2\}_3]$ over the temperature range from 10 to 400 K.

contains five unpaired electrons due to the $S = {}^3/_2$ metal ion and two semiquinone radicals, and the trimeric molecule may contain 15 unpaired electrons. Magnetic moments for the complex reflect the effects of the magnetic exchange between the radical ligands and the paramagnetic $S = {}^3/_2$ cobalt ion. The Co^{III}/Co^{II} transition in the solid state occurs over a very broad temperature range (eq 1), which may be indebted to the delicate

$$[N_3P_3(3,2\text{-Obpy})_3\{Co^{III}(3,6\text{-dbsq})(3,6\text{-dbcat})\}_3] \rightleftharpoons [N_3P_3(3,2\text{-Obpy})_3\{Co^{II}(3,6\text{-dbsq})_2\}_3] \quad (1)$$

planar/skew change in conformation of the bipyridyl unit. The extrapolative slope of μB vs T is directed toward the effects of magnetic exchange between the radical ligands and the paramagnetic $S = {}^3/_2$ metal ion. However, metal dσ and dπ electrons interact differently with the unpaired 3,6-dbsq π spins of the $Co^{II}(3,6\text{-dbsq})_2$ species, and the resulting spin states may contribute to the complicated magnetic behavior of the Co^{II} forms at high temperature.[13] The temperature dependence of the magnetic moment is the result of shifts in equilibria. As radical based $S = {}^1/_2$ molecules they show EPR spectra that are centered near $g = 2.00$, with ^{59}Co ($I = {}^7/_2$) hyperfine coupling. In toluene glass (77 K) the spectra show slight anisotropy, an effect that is common for delocalized organic radicals.[23] The anisotropic spectrum of $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,6\text{-dbbq})_2\}_3]$ is shown in Figure 4; the signal is essentially the spectrum of a ligand-based radical in $[N_3P_3(3,2\text{-Obpy})_3\{Co^{III}(3,6\text{-dbsq})(3,6\text{-dbcat})\}_3]$. It consists of two components, $g_1 = 2.0098$ and $g_2 = 2.0004$, each coupled to the cobalt nucleus with constants of $A_1 = 34$ G and $A_2 = 25$ G. In contrast, above room temperature only a broad first-derivative signal was observed. This could occur by transformation between two redox isomers (Co(III)/Co(II))[24] at room temperature.

Electronic spectra recorded in solution show features that are characteristic of the Co(III) and Co(II) charge distribution. Prominent bands that appear in the electronic spectra of the

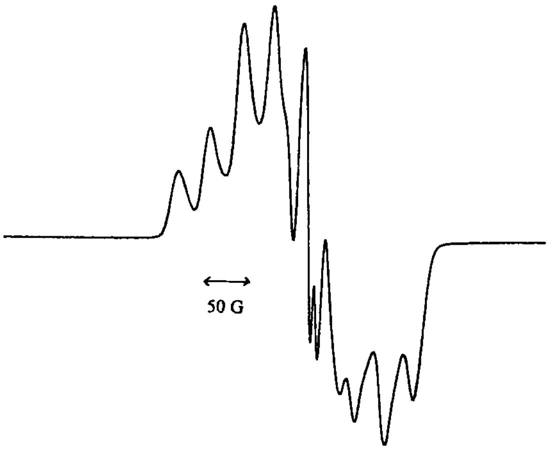


Figure 4. EPR spectrum of $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,6\text{-dbbq})_2\}_3]$ recorded in a toluene glass at 77 K.

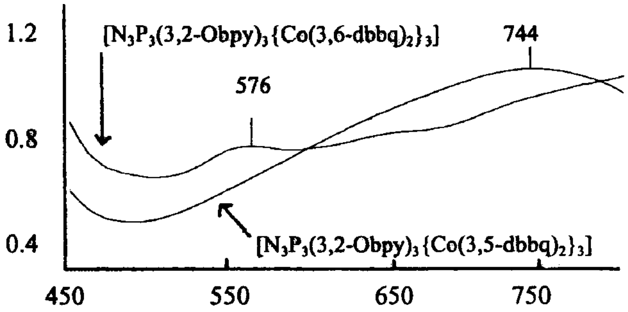


Figure 5. Electronic spectra of $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,6\text{-dbbq})_2\}_3]$ and $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,5\text{-dbbq})_2\}_3]$ in toluene solution ($C = 2.0 \times 10^{-4}$ M).

present two complexes are shown in Figure 5. $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,5\text{-dbbq})_2\}_3]$ shows characteristic band at 744 nm (1.3×10^3 M^{-1} cm^{-1}). In contrast, $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,6\text{-dbbq})_2\}_3]$ shows a band in the 540−600 nm range of the visible region while the band at 744 nm is decreased. The high energy absorption band appeared characteristically for Co(III) in the system.[13] Thus, the solution spectra show that for $[N_3P_3(3,2\text{-Obpy})_3\{Co(3,6\text{-dbbq})_2\}_3]$, a mixture of Co(III) and Co(II) species exist at equilibrium and for the 3,5-dbbq analogue, the Co(II) species predominates in the solution. Such a finding is consistent with the IR spectra.

In conclusion, new tris(bidentate) donor ligands attached to cyclotriphosphazene skeleton have been prepared and characterized. A rationally designed trinuclear cobalt complex, $[N_3P_3(3,2\text{-Obpy})_3\{Co(dbbq)_2\}_3]$, is significant as an unusual structure in that it shows exocyclic ring effects around room temperature. The present ligands may be used to construct elaborate structures containing three remote metal centers that exhibit desirable behavior.

Acknowledgment. This research was supported financially by the Ministry of Science and Technology in Korea.

Supporting Information Available: An X-ray crystallographic file in CIF format for $N_3P_3(3,2\text{-Obpy})_3$ is available free of charge via the Internet (http://pubs.acs.org).

IC990215D

---

[23] Bresgunov, A. Y.; Dubinsky, A. A.; Poluektov, O. G.; Lebedev, Y. S.; Prokof'ev, A. I. *Mol. Phys.* **1992**, *75*, 1123.

[24] Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1981**, *102*, 4951.