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A Trinucleating Oxygen-Containing Ligand with Two Different Coordination Sites and Its Heterotrinuclear Complexes

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Linear heterotrinuclear complexes of the type UO_2–M–UO_2 (M = Co, Ni, Zn) with the trinucleating synthesis-directing ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$) of formula $[(UO_2)_2M(bhpp)_2]\cdot 6py$ (py = pyridine) are reported. These compounds are synthesized from the corresponding isomerically pure mononuclear precursors $M(bhppH_2)_2$ (M = Ni, Co, Zn) by treating them with uranyl acetate in a strong basic medium. The molecular structures of two of these compounds, UO_2–M–UO_2, have been solved by X-ray diffraction methods. Crystal data for M = Co: triclinic, space group $P\bar{1}$, with $a = 9.919$ (5) Å, $b = 11.597$ (8) Å, $c = 12.789$ (3) Å, $\alpha = 93.02$ (4)°, $\beta = 92.58$ (3)°, $\gamma = 106.67$ (5)°, $V = 1404.6$ Å^3, $Z = 1$, $D_x = 1.89$ g·cm^{-3}, μ(Mo Kα) = 58 cm^{-1}, and $F(000) = 757$. Crystal data for M = Ni: triclinic, space group $P\bar{1}$, with $a = 9.903$ (6) Å, $b = 11.587$ (3) Å, $c = 12.788$ (7) Å, $\alpha = 93.17$ (3)°, $\beta = 92.28$ (6)°, $\gamma = 106.41$ (4)°, $V = 1403.2$ Å^3, $Z = 1$, $D_x = 1.87$ g·cm^{-3}, μ(Mo Kα) = 59 cm^{-1}, and $F(000) = 758$.

Introduction

As a part of our research program about polynuclear complexes and synthesis-directing polynucleating ligands, we have focused our interest in trinucleating ligands in order to synthesize linear heterotrinuclear complexes of the type M–M′–M or M′–M–M′. As such, these compounds should furnish an unusual opportunity to investigate the cooperative effect of unlike metal ions in close proximity that would be observable in the chemical and physical properties of the resulting compounds (in catalysis, magnetochemistry studies, etc.)

A number of trinuclear complexes have been characterized and reported in the literature. Most of them are formed by a chelating ligand, L, forming mononuclear complexes of the type ML_2. These mononuclear complexes acting as ligands toward transition-metal ions afford homo or heterotrinuclear complexes of formula $[ML_2]_2M'$. Only a few trinuclear complexes have been described with a true trinucleating ligand.

The design and preparation of heteropolynuclear complexes with trinucleating ligands present some interesting problems. To accomplish a controlled synthesis one must be able to direct different metal ions, with specificity, to different binding sites within the ligand molecule.

Recently, Lintvedt and coworkers have reported interesting linear trinuclear complexes of the type UO_2–M–UO_2 (M = Mn, Fe, Co, Ni, Co, Zn).[1] The molecular structures of the Ni, Fe, Mn, and Co complexes were also reported. In his work Lintvedt and co-workers use a tetraketone, 1,7-diphenyl-1,3,5,7-heptanetetrone, as a trinucleating ligand, and the synthesis of the trinuclear complexes starts from a controlled mixture of uranyl acetate and the other appropriate metal acetate. Two uranyl ions are directed to the outer positions of the ligand and the central site is reserved for the other metal ion. All metal ions are also coordinated by pyridine molecules. Uranium atoms are seven-coordinated by six oxygen and one nitrogen atom of one coordinated pyridine. The specificity of this controlled synthesis is achieved because the outer positions are the only ones accessible to take into account the unusual seven-coordination of the uranium atoms in these compounds, according to Lintvedt's suggestion.

Our approach, in order to obtain specificity in the synthesis of trinuclear complexes with trinucleating ligands, is different. We tried polynucleating ligands with different reactivities in their coordinating sites, like the compound 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$) (Figure 1). With this ligand we are able to synthesize pure monomeric complexes,[2-4] the divalent metal ion occupying the most reactive inner site, allowing the two symmetric and less reactive outer sites to react with other metal ions in a following reaction, as is evident from the molecular structure shown by these mononuclear complexes.[2] In this paper we report the synthesis, characterization, and molecular structure by X-ray diffraction methods of some heterotrinuclear complexes of this ligand of the type UO_2–M–UO_2.

Experimental Section

Ligand Synthesis. The ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$) was prepared by following literature methods.[3,5]

Synthesis of the Complexes. The mononuclear complexes $Zn(bhppH_2)_2\cdot 2MeOH$, $Co(bhppH_2)_2\cdot 2MeOH$, and $Ni(bhppH_2)_2\cdot 2MeOH$ were prepared as already described by us.[2,3]

UO_2–Zn–UO_2 Complex. To a solution of $Zn(bhppH_2)_2\cdot 2MeOH$ (0.300 g) in a mixture of methanol (30 mL) and triethylamine (15 mL) was added dioxouranium(VI) acetate dihydrate (0.473 g) dissolved in methanol (10 mL). An orange yellow precipitate was obtained, which was filtered, washed with methanol, and dried. Yield: 0.350 g.

UO_2–Co–UO_2 Complex. To a solution of $Co(bhppH_2)_2\cdot 2MeOH$ (0.286 g) in a mixture of methanol (50 mL), tetrahydrofurane (2 mL), and triethylamine (25 mL) was added dioxouranium(VI) acetate dihydrate (0.416 g). A dark red precipitate was obtained, which was filtered, washed with methanol, and dried. Yield: 0.080 g. By evaporation of the mother liquor, another portion of the red complex was obtained (0.080 g).

UO_2–Ni–UO_2 Complex. To a solution of $Ni(bhppH_2)_2\cdot 2MeOH$ (0.300 g) in a mixture of methanol (30 mL) and triethylamine (22 mL) was added dioxouranium(VI) acetate dihydrate (0.450 g). A red yellow precipitate was obtained, which was filtered, washed with methanol, and dried. Yield: 0.330 g.

We have not been able to obtain these compounds in an analytically pure form. The analytical results approach the expected values but clearly indicate that these compounds are not pure.

All compounds were purified by slow evaporation of a pyridine solution of the trinuclear complexes. The crystalline solids obtained were pyridine adducts of formula $[(UO_2)_2M(bhpp)_2]\cdot 6py$, and their analyses were correct in all cases.

Single crystals appropriate for X-ray diffraction methods were obtained by slow diffusion of methanol in a pyridine solution of the trinuclear compounds in the refrigerator.

Spectral Measurements. IR spectra were obtained on a Perkin-Elmer FT Spectrophotometer as KBr pellets.

Crystallography and Structure Determination. Uranyl–Cobalt–Uranyl Complex. A dark-red prismatic crystal of $C_{50}H_{38}N_4O_{12}U_2Co\cdot 2C_5H_5N$ was selected for X-ray diffraction analysis, being triclinic, space group $P\bar{1}$, with $a = 9.919$ (5) Å, $b = 11.597$ (8) Å, $c = 12.789$ (3) Å, $\alpha = 93.02$

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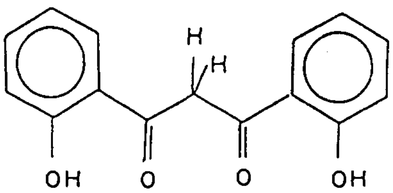

Figure 1. 1,3-Bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$).

(4)°, β = 92.58 (3)°, γ = 106.67 (5)°, V = 1404.6 $Å^3$, Z = 1, D_x = 1.89 $g{\cdot}cm^{-3}$, μ(Mo Kα) = 58 cm^{-1}, and F(000) = 757.

X-ray diffraction data were collected with an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 293 K on a 0.11 × 0.12 × 0.20 mm crystal. A total of 4063 unique reflections with $\theta \leq 25°$ were obtained from which 1980 were considered observed with $F > 2.5\sigma(F)$. The range of hkl was $-11 \leq h \leq 11$, $-13 \leq k \leq 13$ and $0 \leq l \leq 14$. No significant decay of standard reflections intensities was observed (0.8%). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The position of the U atom was found by Patterson methods with the ROTSEARCH/87 program.[6] The remaining non-hydrogen atoms were located by successive weighted F_0 syntheses. Refinements were performed with the SHELX76 program[7] using anisotropical thermal parameters. Due to the poor quality of the diffraction data a final R value of 0.107 was achieved. The maximum and minimum heights in the final difference Fourier synthesis are 5.0 and -3.0 $e{\cdot}Å^{-3}$ near the U atom (at 1.15 Å).

Uranyl-Nickel-Uranyl Complex. A single crystal of $C_{50}H_{38}N_4O_{12}U_2Ni{\cdot}2C_5H_5N$ was selected for X-ray diffraction analysis, being triclinic, space group $P\bar{1}$, with a = 9.903 (6) Å, b = 11.587 (3) Å, c = 12.788 (7) Å, α = 93.17 (3)°, β = 92.28 (6)°, γ = 106.41 (4)°, V = 1403.2 $Å^3$, Z = 1, D_x = 1.87 $g{\cdot}cm^{-3}$, μ(Mo Kα) = 59 cm^{-1}, and F(000) = 758.

X-ray diffraction data were collected with an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at 293 K on a 0.10 × 0.12 × 0.19 mm prismatic crystal. A total of 4915 unique reflections with $\theta \leq 25°$ were obtained from which 4040 were considered observed with $F > 2.5\sigma(F)$. The range of hkl was $-11 \leq h \leq 11$, $-13 \leq k \leq 13$ and $0 \leq l \leq 14$. No significant decay of standard reflections intensities was observed (0.8%). The intensities were corrected for Lorentz and polarization effects, but not for absorption.

The similarity of these crystal parameters with those corresponding to the aforementioned U–Co–U complex suggested possible isomorphism between them; consequently, starting atom positions for the refinement were directly taken from the previously solved compound.

The refinements were carried out with the least-squares full-matrix SHELX76 program.[7] Non-hydrogen atoms were refined anisotropically, except for interstitial pyridine molecule atoms, which were refined isotropically. The final R and R_w values were 0.061 and 0.057, respectively, with $w = 1/[\sigma^2(F) + 0.00776F^2]$. The maximum and minimum heights in the final difference Fourier synthesis are 2.7 and -2.5 $e{\cdot}Å^{-3}$ near the U atom (at 0.95 Å). The scattering factors were taken from ref 8 in both cases.

Results and Discussion

General Chemistry. The compound 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$) is an excellent ligand to yield pure mononuclear complexes with divalent transition-metal ions of formula $M(bhppH_2)_2$[3] (eq 1).

$$bhppH_3 + M(AcOO)_2 \rightarrow M(bhppH_2)_2 + AcOOH \qquad (1)$$

The divalent metal ion is coordinated in a square-planar fashion by two β-diketone moieties, corresponding to two $bhppH_2^-$ ligands. Usually the coordinated metal fixes two solvent molecules to achieve the hexacoordination.[9]

On the other hand, the anionic complex $[Li(bhppH_2)_2]^-$ exhibits a tetrahedral coordination,[4] while the Cr(III) and Fe(III) compounds present an octahedral coordination around the metal ion.[10]

Table I. Final Fractional Atomic Coordinates (×10^4) with Esd's and Equivalent Temperature Factors for $[UO_2NiUO_2(bhpp)_2]{\cdot}6py$

	x/a	y/b	z/c	B_{eq}, $Å^2$
U	1232 (1)	−583 (0)	2538 (0)	2.89
Ni	0 (0)	0 (0)	0 (0)	2.53
O1	2061 (8)	1288 (8)	3271 (7)	4.09
O2	412 (8)	848 (6)	1443 (6)	2.92
O3	511 (7)	−1388 (6)	656 (6)	2.95
O4	652 (9)	−2605 (7)	2388 (6)	3.99
O5	−422 (9)	−773 (8)	3116 (7)	3.96
O6	2920 (8)	−413 (8)	2043 (7)	4.19
N1	2147 (9)	791 (8)	−352 (7)	3.23
C2	1380 (16)	2469 (13)	4603 (10)	4.75
C3	573 (20)	3200 (14)	4930 (12)	5.91
C4	−396 (16)	3528 (12)	4206 (10)	4.74
C5	−472 (15)	3073 (11)	3152 (11)	4.28
C6	342 (12)	2321 (9)	2795 (9)	3.16
C1	1235 (13)	2015 (12)	3547 (9)	3.73
C7	209 (10)	1884 (9)	1683 (9)	2.85
C8	−192 (12)	2600 (10)	953 (9)	3.21
C9	595 (11)	−2335 (9)	127 (9)	2.78
C11	1829 (12)	−3934 (10)	45 (11)	3.73
C12	2427 (13)	−4754 (11)	516 (14)	4.97
C13	2409 (15)	−4850 (12)	1601 (13)	4.93
C14	1798 (14)	−4123 (11)	2225 (11)	4.29
C15	1212 (11)	−3273 (9)	1754 (10)	3.23
C10	1215 (11)	−3183 (10)	666 (9)	3.15
C16	2907 (13)	115 (13)	−801 (12)	4.83
C17	4257 (13)	594 (14)	−1091 (13)	5.46
C18	4905 (14)	1805 (15)	−912 (16)	6.18
C19	4173 (20)	2469 (16)	−374 (23)	9.87
C20	2748 (16)	1946 (14)	−165 (16)	6.56
C21	2172 (14)	−448 (12)	5167 (10)	4.07
C22	2898 (17)	−487 (13)	6121 (11)	5.06
C23	3960 (19)	−1062 (16)	6092 (12)	5.99
C24	4155 (16)	−1629 (13)	5150 (12)	5.11
C25	3411 (14)	−1548 (13)	4255 (12)	4.85
N2	2384 (12)	−929 (11)	4270 (9)	4.64
N3	5127 (36)	3929 (31)	3042 (26)	16.14
C26	6409 (37)	4185 (32)	2411 (26)	12.78
C27	7137 (30)	5260 (28)	2455 (23)	10.80
C28	6729 (34)	6282 (28)	2912 (26)	11.91
C29	5596 (35)	6071 (31)	3509 (25)	12.33
C30	4930 (30)	4831 (29)	3556 (24)	11.0o

This compound, $bhppH_3$, is also a potentially trinucleating ligand with two different coordination sites. The central site is chemically comparable to one β-diketone moiety and its reactivity is also similar[3] as has been already reported. The outer sites have ketonic and phenolic coordinating oxygen atoms and their reactivities are lower than that corresponding to the inner site.

One of the most important problems in the synthesis of heteropolynuclear complexes is the purity of the mononuclear precursors. In this case the problem is minimized by the high reactivity of the central coordinating site in comparison with the exterior sites. Due to its planar structure, only the mononuclear complexes with divalent metal ions are able to afford polynuclear compounds. These are synthesized by treating the mononuclear precursors with a different (heterotrinuclear) or alike (homotrinuclear) metallic salt in a strong basic medium to deprotonate the phenolic groups (eq 2).

$$M(bhppH_2)_2 + 2M'X_2 \xrightarrow[\text{base}]{} [M'MM'(bhpp)_2] + 4HX \qquad (2)$$

The synthetic experimental conditions are critical because mixtures of homotrinuclear compounds, $[MMM(bhpp)_2]$ or $[M'M'M'(bhpp)_2]$, could be obtained due, probably, to the strong basic medium employed. In our case, by introduction of slight changes in these conditions, a large series of compounds from red to yelloy color have been obtained, corresponding to mixtures of $[CoCoCo(bhpp)_2]$ and $[UO_2UO_2UO_2(bhpp)_2]$ complexes.

For metal ions other than UO_2^{2+}, which tend to occupy outer positions and, as indicated, relatively easily give UO_2MUO_2

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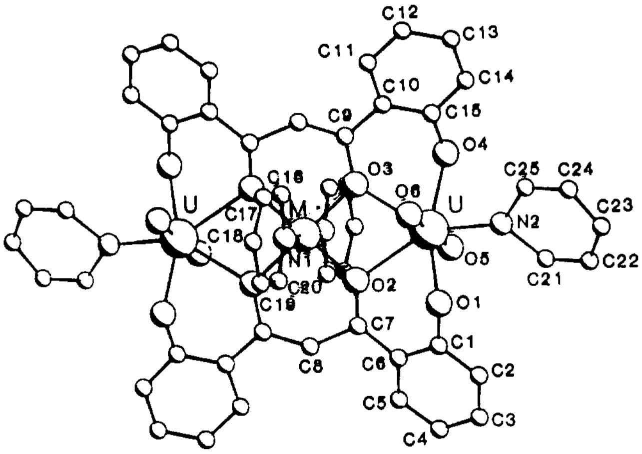

Figure 2. Perspective view of the $[UO_2MUO_2(bhpp)_2]\cdot 6py$ (M = Co, Ni) compounds with the atom numbering.

Table II. Final Fractional Atomic Coordinates ($\times 10^4$) with Esd's and Equivalent Temperature Factors for $[UO_2CoUO_2(bhpp)_2]\cdot 6py$

	x/a	*y/b*	*z/c*	B_{eq}, Å^2
U0	−1228 (1)	571 (1)	−2547 (2)	4.75
C0	0 (0)	0 (0)	0 (0)	4.88
O1	2057 (23)	1310 (24)	3265 (26)	6.47
O2	451 (21)	873 (19)	1419 (20)	4.16
O3	−518 (23)	1359 (20)	−721 (27)	7.54
O4	−863 (26)	2588 (22)	−2403 (29)	6.85
O5	416 (22)	741 (24)	−3097 (24)	5.59
O6	−2934 (19)	358 (23)	−2043 (23)	5.65
N1	2171 (24)	781 (23)	−401 (27)	4.41
N2	−2403 (28)	900 (31)	−4204 (15)	4.60
N3	−5095 (87)	3897 (79)	3067 (57)	15.19
C1	1191 (39)	2038 (39)	3570 (52)	6.16
C2	1311 (45)	2497 (37)	4572 (41)	4.89
C3	586 (56)	3238 (39)	4861 (44)	7.89
C4	−395 (44)	3485 (40)	4279 (56)	7.34
C5	−493 (40)	3086 (34)	3180 (50)	6.35
C6	333 (33)	2333 (30)	2733 (47)	5.85
C7	187 (31)	1876 (30)	1662 (39)	4.79
C8	−231 (39)	2580 (33)	939 (41)	4.01
C9	−579 (31)	2381 (25)	−74 (35)	2.25
C10	−1216 (31)	3190 (26)	−637 (46)	3.99
C11	−1858 (34)	3958 (32)	−110 (40)	6.03
C12	−2423 (34)	4753 (29)	−615 (51)	5.12
C13	−2336 (41)	4844 (35)	−1635 (51)	5.90
C14	−1770 (40)	4139 (33)	−2170 (42)	6.54
C15	−1240 (34)	3246 (31)	−1723 (43)	2.90
C16	2961 (39)	148 (35)	−749 (46)	7.46
C17	4282 (33)	616 (41)	−1158 (43)	6.74
C18	4935 (36)	1863 (45)	−913 (48)	9.44
C19	4138 (52)	2476 (46)	−580 (80)	19.71
C20	2775 (43)	1903 (46)	−243 (54)	9.45
C21	−2119 (39)	452 (35)	−5162 (42)	3.84
C22	−2859 (53)	430 (38)	−6023 (57)	8.40
C23	−3941 (46)	1100 (44)	−5965 (44)	6.57
C24	−4207 (43)	1532 (44)	−5078 (42)	5.65
C25	−3356 (45)	1506 (39)	−4269 (45)	7.42
C26	6123 (92)	4030 (90)	2377 (72)	18.17
C27	7039 (80)	5136 (83)	2361 (60)	14.58
C28	6597 (90)	6084 (94)	2938 (72)	21.93
C29	5613 (100)	5801 (97)	3613 (75)	14.95
C30	4879 (99)	4740 (117)	3645 (99)	19.23

Table III. Selected Bond Lengths (Å) with Esd's in Parentheses for $[UO_2NiUO_2(bhpp)_2]\cdot 6py$

O1–U	2.228 (8)	O2–Ni	2.012 (7)
O2–U	2.509 (7)	O3–Ni	2.030 (7)
O3–U	2.532 (7)	N1–Ni	2.141 (9)
O4–U	2.244 (8)	C1–O1	1.372 (14)
O5–U	1.785 (8)	C7–O2	1.295 (12)
O6–U	1.774 (8)	C9–O3	1.282 (12)
N2–U	2.554 (11)	C15–O4	1.332 (14)

Table IV. Selected Bond Lengths (Å) with Esd's in Parentheses for $[UO_2CoUO_2(bhpp)_2]\cdot 6py$

O1–U	2.229 (24)	O2–Co	1.998 (24)
O2–U	2.524 (31)	O3–Co	2.043 (21)
O3–U	2.458 (34)	N1–Co	2.179 (24)
O4–U	2.239 (25)	C1–O1	1.419 (51)
O5–U	1.768 (22)	C7–O2	1.289 (40)
O6–U	1.793 (19)	C9–O3	1.427 (43)
N2–U	2.472 (10)	C15–O4	1.376 (49)

Table V. Selected Bond Angles (deg) with Esd's in Parentheses for $[UO_2NiUO_2(bhpp)_2]\cdot 6py$

O2–U–O1	70.3 (3)	N1–Ni–O2	89.7 (3)
O3–U–O1	131.9 (3)	N1–Ni–O3	91.1 (3)
O3–U–O2	66.3 (2)	C1–O1–U	124.3 (7)
O4–U–O1	158.9 (3)	Ni–O2–U	104.5 (3)
O4–U–O2	130.0 (3)	C7–O2–U	131.6 (7)
O4–U–O3	68.9 (3)	C7–O2–Ni	123.8 (7)
O5–U–O1	91.7 (4)	Ni–O3–U	103.2 (3)
O5–U–O2	83.7 (3)	C9–O3–U	132.7 (7)
O5–U–O3	102.9 (3)	C9–O3–Ni	123.5 (7)
O5–U–O4	85.8 (3)	C15–O4–U	126.2 (7)
O6–U–O1	87.6 (4)	C7–C6–C5	120 (1)
O6–U–O2	99.5 (3)	C7–C6–C1	123 (1)
O6–U–O3	80.2 (3)	C2–C1–O1	116 (1)
O6–U–O4	93.5 (4)	C6–C1–O1	121 (1)
O6–U–O5	176.3 (4)	C6–C7–O2	119 (1)
N2–U–O1	78.1 (3)	C8–C7–O2	124 (1)
N2–U–O2	147.7 (3)	C8–C7–C6	117 (1)
N2–U–O3	145.3 (3)	C10–C9–O3	118 (1)
N2–U–O4	81.1 (3)	C14–C15–O4	117 (1)
N2–U–O5	91.3 (4)	C10–C15–O4	123 (1)
N2–U–O6	85.0 (4)	C11–C10–C9	118 (1)
O3–Ni–O2	86.0 (3)	C15–C10–C9	123 (1)

Table VI. Selected Bond Angles (deg) with Esd's in Parentheses for all Non-Hydrogen Atoms for $[UO_2CoUO_2(bhpp)_2]\cdot 6py$

O2–U–O1	70 (1)	N1–Co–O2	90 (1)
O3–U–O1	131 (1)	N1–Co–O3	89 (1)
O3–U–O2	66 (1)	C1–O1–U	124 (2)
O4–U–O1	159 (1)	Co–O2–U	104 (1)
O4–U–O2	130 (1)	C7–O2–U	131 (2)
O4–U–O3	69 (1)	C7–O2–Co	124 (3)
O5–U–O1	91 (1)	Co–O3–U	105 (1)
O5–U–O2	84 (1)	C9–O3–U	137 (2)
O5–U–O3	102 (1)	C9–O3–Co	117 (3)
O5–U–O4	87 (1)	C15–O4–U	125 (2)
O6–U–O1	87 (1)	C7–C6–C5	124 (4)
O6–U–O2	97 (1)	C7–C6–C1	126 (4)
O6–U–O3	80 (1)	C2–C1–O1	119 (4)
O6–U–04	95 (1)	C6–C1–O1	116 (5)
O6–U–O5	177 (1)	C6–C7–O2	120 (3)
N2–U–O1	179 (1)	C8–C7–O2	124 (4)
N2–U–O2	148 (1)	C8–C7–C6	116 (3)
N2–U–O3	145 (1)	C10–C9–O3	113 (4)
N2–U–O4	81 (1)	C14–C15–O4	116 (5)
N2–U–O5	94 (1)	C10–C15–O4	125 (3)
N2–U–O6	84 (1)	C11–C10–C9	122 (5)
O3–Co–O2	84 (1)	C15–C10–C9	123 (3)

heterotrinuclear compounds, the boiling temperature used and the relatively long time required to dissolve the mononuclear complex in the presence of a large concentration of triethylamine should favor reorganization to yield homotrinuclear complexes. To minimize this reorganization problem, with metals other than UO_2^{2+} cations, we are currently employing NaH in dry THF (tetrahydrofuran) at room temperature. The results seem to be satisfactory, although again, no analytically pure heterotrinuclear complexes are obtained. Surprisingly when these heterotrinuclear complexes (CoNiCo, CoZnCo, MnCoMn, MnZnMn) are treated with pyridine, *outer* homodinuclear complexes are obtained, leaving a vacancy in the central position, the ligand's more reactive position as evidenced by X-ray diffraction analyses.[11]

Structure of $[UO_2MUO_2(bhpp)_2]\cdot 6py$ (M = Co, Ni) Complexes. Since the molecular structures of both compounds are identical,

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[11] Teixidor, F.; Colomer, J.; Casabó, J.; Miravitlles, C. To be submitted for publication.

only one of them is presented (Figure 2).

The positional parameters for all non-hydrogen atoms of both compounds are listed in Tables I and II. Selected bond distances and angles are reported in tables III–VI, respectively.

The tetragonally distorted octahedrally coordinated divalent metal ion, M (M = Ni Co), is placed at the crystallographic inversion center. It is coordinated with two pyridine groups in the axial direction and by four oxygen atoms of the β-diketone moieties of the two $bhpp^{3-}$ ligands in the basal plane. The M–O bond lengths are quite normal for high-spin Ni(II) and Co(II) metal ions. Both exhibit almost the same metal–oxygen distance (2.020 Å on average) as in the case of Lintvedt's complexes.[1] Similar distances are found in simple acetylacetonate complexes, $M(acac)_2$.[12-14] The M–N axial bond distance slightly increase in the order Ni < Co (2.141 and 2.179 Å, respectively).

The uranyl ions occupy the outer coordination positions with two ketonic oxygens, two phenolic oxygens, and one pyridine nitrogen comprising the five equatorial donor atoms in a distorted-pentagonal-bipyramidal coordination sphere geometry. The bond distances and angles around the uranium atoms in both commpounds are virtually identical. The by symmetry identical U–Ni and U–Co distances are 3.587 (3) Å in both cases.

The ligand molecule and the three metal atoms are essentially coplanar. Two additional pyridine molecules are occupying interstitial lattice positions.

The most significant conclusion to draw from the structural results is that the ligand molecule is able to accommodate with little trouble three metal ions showing a polynucleating behavior. The flexibility of the carbon backbone is sufficient to permit metal–oxygen bond lengths as different as the ≃2.50 Å observed for U–O and the ≃2.02 Å in M–O (M = Ni, Co). This is accomplished by forcing the ends of the ligands out so that the four oxygens atoms (the two ketonics and the two phenolics) of each molecule are not linear, as is evident in Figure 2. On the other hand the synthesis-directing capacity is emphasized in the formation of mononuclear complexes and heterotrinuclear complexes of the type M′–M–M′.

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Registry No. $[(UO_2)_2Co(bhpp)_2]\cdot6py$, 118474-61-6; $[(UO_2)_2Ni(bhpp)_2]\cdot6py$, 118474-63-8; $[(UO_2)_2Zn(bhpp)_2]\cdot6py$, 118474-64-9; $Zn(bhppH_2)_2\cdot2MeOH$, 118474-65-0; $Co(bhppH)_2\cdot2MeOH$, 93401-36-6; $Ni(bhppH_2)_2\cdot2MeOH$, 118474-66-1.

Supplementary Material Available: Listings of anisotropic thermal parameters (2 pages); listings of observed and calculated structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

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Phosphoranide Ligands with Variable Coordination Modes. Synthesis, Properties, and X-ray Crystal Structures of $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$ and $[(H_2cyclenP)PtCl_2PPh_3]Cl$

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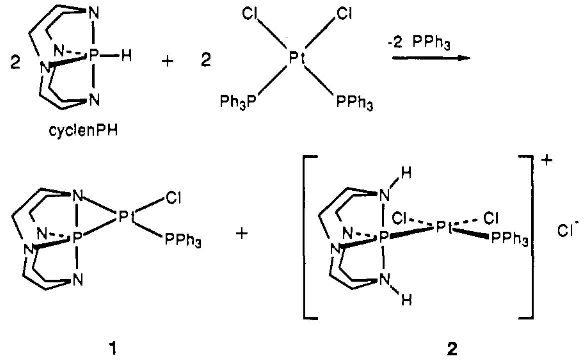
The complex $(\eta^2\text{-cyclenP})Pt(Cl)PPh_3$ (**1**) is readily formed by the deprotonation of $[(H_2cyclenP)PtCl_2PPh_3]Cl$ (**2**) with NaOH in CH_2Cl_2. Both complexes contain phosphoranide ($R_4P{:}^-$) ligands. Complex **1** reacts with HBF_4 to give the monoprotonated derivative $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$ (**3**), a species in which one of the P–N bonds of the cyclenP unit is cleaved and the proton is attached to that nitrogen. Treatment of **3** with HCl in THF gives $[(H_2cyclenP)PtCl_2PPh_3]BF_4$ (**4**) (which contains a cation identical with that of **2**), while treatment of **3** with NaCl in Me_2SO leads to **1** and **2** via disproportionation. The X-ray crystal structures of **2** and **3** were obtained. Data for **2** indicate that the axial nitrogens are protonated and the cyclenP unit is oriented with its P–N axial bonds perpendicular to the platinum coordination plane. Data for **3** show that the HcyclenP unit is coordinated to the platinum via phosphine and amine linkages and that the phosphorus is four-coordinate. X-ray data: $C_{26}N_4P_2Cl_3Pt$ (**2**), orthorhombic, space group *Pcab*, $a = 15.391$ (4) Å, $b = 17.021$ (6) Å, $c = 25.226$ (14) Å, $Z = 8$, $R = 0.087$, $R_w = 0.089$; $C_{26}H_{31}BN_4F_4P_2ClPt$ (**3**), monoclinic, space group $P2_1/c$, $a = 14.873$ (3) Å, $b = 13.021$ (3) Å, $c = 15.723$ (3) Å, $\beta = 106.654$ (14)°, $Z = 4$, $R = 0.044$, $R_w = 0.046$.

We recently reported the synthesis of the new phosphoranide[1,2] complexes $(\eta^2\text{-cyclenP})Pt(Cl)PPh_3$ (**1**) and $[(H_2cyclenP)PtCl_2PPh_3]Cl$ (**2**) according to reaction 1.[3a,b] In addition, we found that **1** could be converted directly to **2** by reaction with HCl. However, attempts to isolate a monoprotonated intermediate in this conversion were unsuccessful since addition of less than 2 equiv of HCl led to only **2** and unreacted **1**. Moreover, a monoprotonated adduct of **1** may be important in reaction 1 as well. Isolation of this species is important to the understanding of the mechanism of the syntheses and reactions of transition-metal complexes with phosphoranide ligands.[3] We herein report (1) the synthesis, reactions, NMR properties, and X-ray crystal structure of a monoprotonated adduct of **1**, $[(\eta^2\text{-HcyclenP})Pt(Cl)PPh_3]BF_4$



(1)

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