SUPPORTING INFORMATION

for

Bin-Salamon, Brewer, Depperman, Franzen, Kampf, Kirk, Kumar, Lappi, Peariso, Preuss, and Shultz "Bridge-mediated Differences in Dinuclear Valence Tautomeric Behavior"

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Table 1. Crystal data and structure refinement for **1** and **2**.

Empirical formula	$C_{82}H_{98}N_4O_8Co_2$•(**1**•$2C_7H_8$)	$C_{107}H_{130}N_4O_8Co_2$ (**2**•$3C_7H_8$)
a/Å	16.862(3)	20.633(4)
b/Å	26.337(5)	19.207(3)
c/Å	26.737(5)	24.055(4)
β/deg	124.136(3)	95.452(7)
V/Å^3	9828(3)	9490(3)
Z	4	4
Formula weight	1641.88	1718.01
Crystal system, space group	monoclinic, $P2_1/c$ (purple plate)	Monoclinic, $P2_1/n$ (purple block)
T/K	123(2)	133(2)
/Å	0.71073	0.71073
$_{calc}$/g cm^{-3}	1.110	1.202
/cm^{-1}	3.91	4.08
$R1^d$	0.0755^c	0.0753^d
$wR2^b$	0.1447^c	0.1692^d

^{a}Quantity minimized = R = $\Sigma||F_o|-|F_c||/ \Sigma|F_o|$. ^{b}wR2 = $\Sigma[w(F_o^2-F_c^2)^2]/ \Sigma[(wF_o^2)^2]^{1/2}$. ^{c}w = $1/[\sigma^2(F_o^2) + (0.0475P)^2 + 0.00P]$, P = $[2F_c^2 + F_o^2)]/3$. ^{d}w=$1/[\sigma^2(F_o^2)+(0.1057P)^2+8.8966P]$, P=$(F_o^2+2F_c^2)/3$.

Structure Determination.

Purple plate-like crystals of **1** were crystallized from a methylene chloride / toluene solution at 23 deg. C. A crystal of dimensions 0.14 x 0.14 x 0.06 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 128(2) K; the detector was placed at a distance 4.959 cm from the crystal. A total of 1808 frames were collected with a scan width of 0.3° in ω and an exposure time of 120 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 41930

reflections to a maximum 2θ value of 39.98° of which 8974 were independent and 4012 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 721 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package using the space group P2(1)/c with Z = 4 for the formula $C_{100}H_{122}N_4O_9Co_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0755 and wR2 = 0.1612 [based on I > 2sigma(I)], R1 = 0.1447 and wR2 = 0.1618 for all data. Additional details are presented in Table 1 and are given as Supporting information as a CIF file.

Sheldrick, G.M. SHELXTL, v. 5.10; Bruker Analytical X-ray, Madison, WI, 1997.
Sheldrick, G.M. SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 1996.
Saint Plus, v. 6.02, Bruker Analytical X-ray, Madison, WI, 1999.
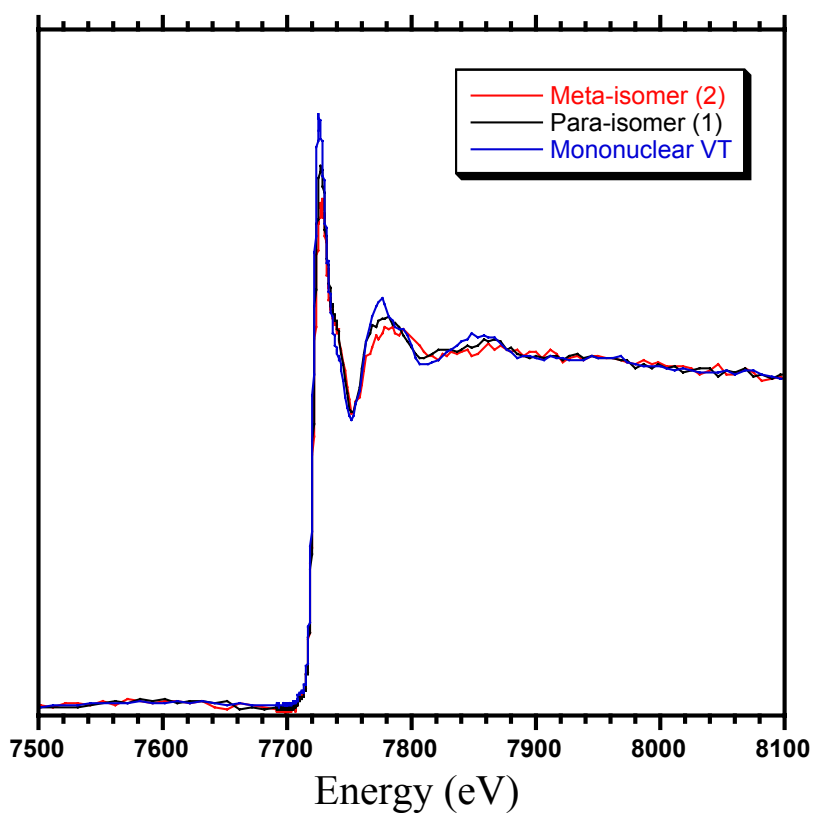
Structure Determination.
Purple block-like crystals of **2** were crystallized from a dichloromethane/toluene solution at 23 deg. C. A crystal of dimensions 0.12 x 0.12 x 0.08 mm was mounted on a standard Bruker SMART CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 138(2) K; the detector was placed at a distance 4.959 cm from the crystal. A total of 2527 frames were collected with a scan width of 0.3° in ω and phi with an exposure time of 90 s/frame. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 53173 reflections to a maximum 2θ value of 40.67° of which 9277 were independent and 4813 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 3009 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection. The data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 5.10) software package using the space group P2(1)/n with Z = 4 for the formula $C_{86}H_{106}N_4O_8Co_2•(C_7H_8)_3$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0753 and wR2 = 0.1692 [based on I > 2sigma(I)], R1 = 0.1606 and wR2 = 0.2217 for all data. Additional details are presented in Table 1 and are given as Supporting information as a CIF file.

Sheldrick, G.M. SHELXTL, v. 5.10; Bruker Analytical X-ray, Madison, WI, 1997.

Sheldrick, G.M. SADABS. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 1996.

Saint Plus, v. 6.02, Bruker Analytical X-ray, Madison, WI, 1999.

XAS Standardization

This figure shows the X-ray absorption spectra for **1** (black), **2** (red), and Co^{III}(3,5-DBSQ)(3,5-DBCat)(py) (blue) at 10 K in poly[styrene] matrices. Since Co^{III}(3,5-DBSQ)(3,5-DBCat)(py) is known to be in the Co^{III} form at 10 K,[1] and since the spectra overlay with the dimeric VT complexes, The dimeric VT complexes **1** and **2** are both in the $Co^{III}Co^{III}$ form at 10 K.

1. Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 4951.