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A Trinuclear Aqua Cyano-Bridged Ruthenium Complex $[\{(\eta^5\text{-}C_5H_5)(PPh_3)_2\text{-}Ru(\mu\text{-}CN)\}_2RuCl_2(PPh_3)(H_2O)]PF_6$: Synthesis, Characterization and Crystal Structure

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The organometallic trinuclear aqua cyano-bridged complex $[\{(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru(\mu\text{-}CN)\}_2RuCl_2(PPh_3)(H_2O)]PF_6$ (**1**), in which the fragment $[RuCl_2(PPh_3)(H_2O)]$ acts as a bridge and an acceptor group between the two terminal cyclopentadienyl ruthenium cyano moieties, was isolated in moderate yield from the reaction of $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$ with $[RuCl_2(PPh_3)_3]$ in THF. To the best of our knowledge, compound **1** is one of the few examples of a trinuclear array of ruthenium fragments bridged by the nitrogen atom of the –C≡N– group (Ru–C≡**N**–Ru′–**N**≡C–Ru) with a Ru-coordinated water molecule. The new aqua complex was structurally characterized by FTIR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, elemental analysis, single-crystal X-ray diffraction, and cyclic voltammetry. The title complex crystallizes in a triclinic unit cell $a = 17.3477(6)$ Å, $b = 17.8551(5)$ Å, $c = 18.2460(7)$ Å, $\alpha = 95.693(2)°$, $\beta = 111.648(2)°$, and $\gamma = 97.839(2)°$ in the space group $P\bar{1}$ with $Z = 2$.

Introduction

Because of their interesting properties (such as conductivity, magnetic and spectral properties), di- and trinuclear complexes with bridging cyanide ligands have been widely studied and have been the object of a large number of publications in the last decades.[1] However, the number of trinuclear complexes reported is less than half of that reported for dinuclear cyanide-bridged complexes, because of difficulties in controlling the synthesis and the ease with which coordination polymers are formed.[2] The bonding characteristics of the cyanide anion make it a good donor at both its C and N atoms[3] – the C atom has a greater affinity for electron-rich metals (such as M^{II}), while the N atom for electron-deficient metals (such as M^{III}). The ability of the cyanide anion to bridge two metal centers and to mediate electronic communications between metal atoms (e.g. electron transfer)[4] led us recently to prepare and determine the X-ray structure of the dinuclear ruthenium cyano-bridged organometallic complex $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru(\mu\text{-}CN)\text{-}Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)]PF_6$.[5] As a natural extension of our previous work, we explored the properties of the –C≡N– bridging group in trinuclear complexes with linear arrays of ruthenium fragments (Ru–C≡**N**–Ru′–**N**≡C–Ru). Vahrenkamp et al.[4c,6] have systematically studied such trinuclear complexes, focusing mainly on the effects of the geometry and the oxidation state at the central metal and of the orientation of the bridges (cyanide vs. isocyanide) on the electronic communication between two terminal metallic fragments. Furthermore, while water is a very common ligand in classical Werner-type coordination chemistry, in 18-electron organometallic complexes coordinated water is relatively rare. This has two main reasons: (a) in organometallic compounds, the metal centers do not display either "hard" or "soft" character, (b) the oxygen atom has a hard donor capacity and binds weakly to most low-valent transition metals like Ru^{II}.[7] These labile complexes are frequently used as precursors for catalysts in organic reactions and in biological applications, viz. aqua complexes of ruthenium have proved to be effective for ring-opening metathesis polymerization (ROMP)[8] and as anti-tumor compounds.[9] In this paper, we report the preparation, structural characterization, and X-ray structure of a rare example of an organometallic trinuclear cyano-bridged ruthenium complex with Ru-coordinated water.

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Results and Discussion

The title organometallic trinuclear aqua complex was readily synthesized by treatment of the electron rich Ru^{II} precursor unit $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$ with 1 equiv. $[RuCl_2(PPh_3)_3]$ in THF in the presence of NH_4PF_6 to yield $[\{(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru(\mu\text{-}CN)\}_2RuCl_2(PPh_3)(H_2O)]PF_6$ (**1**). During the reaction, $[RuCl_2(PPh_3)_3]$, a well-known ruthenium catalyst for hydrogenation catalysis and an important starting material for the preparation of different types of complexes, dissociated extensively in solution[10] and the labile phosphanes were substituted to the central ruthenium unit $[RuCl_2(PPh_3)(H_2O)]$ in complex **1**. The resulting air stable, dark green-blue solid was recrystallized from a mixture of *n*-pentane/dichloromethane/diethyl ether and yielded dark blue crystals suitable for X-ray analysis. The compound was successfully characterized by FTIR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy, mass spectrometry, elemental analysis, and cyclic voltammetry.

The UV/Vis spectrum of **1** (ca. 2×10^{-4} M) was obtained in dichloromethane, chloroform, and dimethylformamide at room temperature and shows intense absorptions in the 250–420 nm region that arise from d–d transitions in the ruthenium moieties that are overlapped by the expected transitions in the aromatic ligands in the UV region. The mono- and the dinuclear compound $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$[5] and $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru(\mu\text{-}CN)Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)]PF_6$,[5] respectively, as well as the starting material $[RuCl_2(PPh_3)_3]$[10b] also show these absorption bands in their spectra. Additionally, a new broad band in the upper limit of the visible region with a tail in the NIR and a maximum at 658 nm (15200 cm^{-1}, ε_{max} = 3937 $M^{-1}\,cm^{-1}$) was also observed (see Figure 1). This was interpreted according to the solvent dependence, bandwidth at half height, shape, and Hush theoretical formalism ($\Delta\nu_{1/2}{}^{\circ}$ = 5925 cm^{-1})[11] as a metal-to-metal charge transfer (MMCT) transition of low intensity from the terminal units $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$ to the central ruthenium fragment $[RuCl_2(PPh_3)(H_2O)]$.[4a,6e] A similar assignment has been made by Matsui et al.[12] in a related trinuclear system $[(NC)(bpy)_2Ru\text{-}CN\text{-}Ru(H_2dcbpy)_2\text{-}NC\text{-}Ru(bpy)_2(CN)]^+$ (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine).

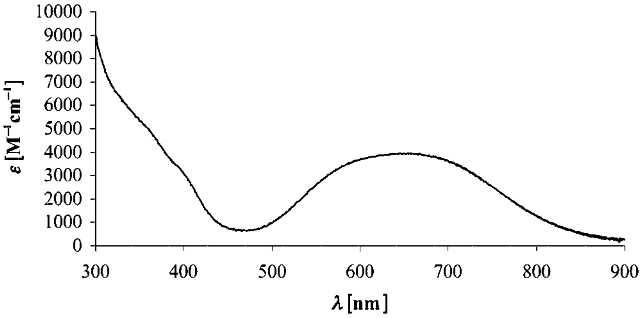

Figure 1. UV/Vis absorption spectrum of **1** (ca. 2×10^{-4} M) recorded in CH_2Cl_2 at room temperature.

The IR spectrum shows two broad bands for the coordinated water at 3056 (υ_{OH}) and 1635 cm^{-1} (δ_{OH})[13] and two sharp bands for the counterion PF_6^- at 841 and 520 cm^{-1}. As expected for a symmetrical cyanide arrangement in trinuclear complexes,[6d] compound **1** shows evidence of only one stretching frequency for the C≡N bonds in the IR spectrum at 2052 cm^{-1}, which occurs at a lower value than those for the mononuclear $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$ and dinuclear $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru(\mu\text{-}CN)Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)]PF_6$ complexes[5] (2072 and 2070 cm^{-1}, respectively). Usually a shift to higher frequency in the position of the ν_{CN} band is expected upon formation of the cyanide-bridged complex because of the kinematic effect (i.e. the restriction of the CN motion by simultaneous coordination of both N and C atoms).[6e] In the present case, a slight weakening of the CN bond can be observed with a band shift of about –20 cm^{-1} relative to the mono- and dinuclear compounds. In spite of the fact that the central ruthenium fragment is a much stronger electron acceptor than the terminal ruthenium centers, this lowering of the position of the ν_{CN} band for the linear array Ru–C≡N–Ru′–N≡C–Ru is probably due to the π-back-donation from the terminal ruthenium to the CN-π* orbitals as well as due to the effect of the electron-donating aqua ligand bonded to the central ruthenium fragment, as was observed for the complex $[RuCl_2(PEt_3)_2(CO)(H_2O)]$.[14] In support of this observation, the ^1H NMR spectrum of the trinuclear complex **1** shows a general deshielding effect when compared with the mononuclear complex $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$; only one singlet of 10 protons for the two cyclopentadienyl ligands, which are deshielded by about 1 ppm, and a singlet at δ = 3.73 ppm for the coordinated water are observed in the spectrum of **1**. The $^{13}C\{^1H\}$ NMR spectrum shows a similar deshielding effect of about 5 ppm for the carbon signal of the CN bond. In the $^{31}P\{^1H\}$NMR spectrum, only two signals of different resonance intensities are observed; the four times more intense signal at δ = 30.0 ppm indicates the equivalency of the four phosphorus nuclei of the terminal ruthenium moieties, and the less intense signal at δ = 17.8 ppm is attributed to the phosphorus atom of the central ruthenium fragment and occurs more downfield relative to the signal arising from the basal *P*Ph₃ group in the five-coordinate structure $[RuCl_2(PPh_3)_3]$ $\{\delta(^{31}P) = 24.1\text{ ppm}\}$.[15] The NMR results show that the $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$ moieties are in a *trans* arrangement, which is also verified by the X-ray analysis (Figure 2). The redox behavior of complex **1** was investigated by cyclic voltammetry in the potential range 0–2.5 V (versus Ag/AgCl) with CH_2Cl_2 as solvent and *n*-Bu_4NPF_6 as the supporting electrolyte. No conclusive information was obtained because of the irreversible character of the observed processes (see Supporting Information).

The central ruthenium fragment is surrounded by six ligands in a slightly distorted octahedral coordination environment with O(48) *trans* to P(94) (Table 2, Figure 2). The Ru–Cl distances (2.327–2.348 Å) are in accordance with the normal, well-established range for Ru^{III} chloride complexes.[16] The central Ru(2)–P(94) bond length (2.292 Å) is slightly shorter than the corresponding bond lengths at the terminal Ru^{II} centers, which is expected for a relatively hard Ru^{III} center. The Ru–H_2O distance (2.215 Å) agrees well

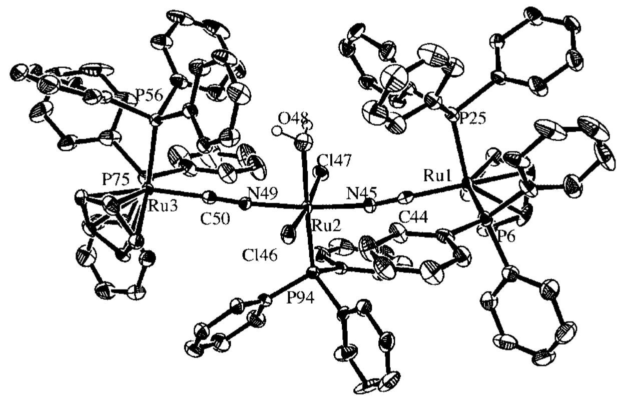

Figure 2. ORTEP[18] drawing at the 50% probability level for the cation of **1**. Solvent molecules and hydrogen atoms, except for the coordinated water, are omitted for clarity.

with the values in similar structural fragments.[16] The H_2O ligand occupies a neat cavity formed by the bulky PPh_3 ligands [P(25) and P(56)]. One of the hydrogen atoms of water shows a weak O–H···π interaction, in which the H(48A)···C(68) distance is 2.52 Å. The Ru–C and Ru–N bond lengths in the terminal pseudo-tetrahedral ruthenium moieties are shorter than those in the dinuclear compound $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru(\mu\text{-}CN)Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)]PF_6$ and in the parent compound $[(\eta^5\text{-}C_5H_5)(PPh_3)_2RuCN]$, and are similar to those in the tetranuclear compound $Cl(CH_3CN)(PPh_3)Ru\{CNCuCl\}\{NCRu(PPh_3)_2Cp\}_2$.[17] A variation in the π-back-donation of the $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru]$ unit can be observed on going from the mono- to the trinuclear complex. The two chlorine ligands are bent towards the water ligand with a Cl(47)–Ru(2)–Cl(46) angle of 171.39°. The cyclopentadienyl ligands are *trans* to each other, and the torsion angle [Ct(1)–Ru(1)–Ru(3)–Ct(2)] between the centroids of the cyclopentadienyl ligands and the metal centers is 123.8°. The most striking feature of the complex is the large deviation from linearity of the Ru–CN–Ru–NC–Ru chain; the Ru(1)–Ru(2)–Ru(3) angle is 164.8°. This is caused by the sterically bulky PPh_3 ligand that induces a steric strain on the other side of the complex – this strain is compensated by the curvature of the M–CN–M–NC–M chain (see Supporting Information). Crystallographic data for complex **1** are collected in Table 1, and the most relevant geometric parameters are shown in Table 2.

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

Empirical formula	$C_{104.34}H_{91.67}F_6N_2P_6Ru_3Cl_{17.91}$
Formula weight	2273.10
Crystal size [mm]	0.15 × 0.15 × 0.20
Temperature [K]	173(2)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a [Å]	17.3477(6)
b [Å]	17.8551(5)
c [Å]	18.2460(7)
α [°]	95.693(2)
β [°]	111.648(2)
γ [°]	97.839(2)
Volume [Å^3]	5134.8(3)
Z	2
Density (calculated) [mg/m^3]	1.480
Absorption coefficient [mm^{-1}]	0.797
F(000)	2300
θ range for data collection [°]	1.54 to 24.70
Index ranges	$-20 \le h \le 20$ $-20 \le k \le 19$ $-21 \le l \le 19$
Reflections collected	47358
Independent reflections	17423 [R(int) = 0.0849]
Absorption correction	none
Data/restraints/parameters	17395/28/1194
Goodness-of-fit on F^2	1.068
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0590, wR_2 = 0.1446
R indices (all data)	R_1 = 0.0996, wR_2 = 0.1681

Table 2. Selected bond lengths [Å] and angles [°] for **1**.

Bond lengths		Angles	
Ru(1)–C(44)	1.972(7)	N(45)–C(44)–Ru(1)	172.5(5)
Ru(1)–Ct(1)	1.885(7)	N(49)–C(50)–Ru(3)	172.6(5)
Ru(1)–P(6)	2.346(2)	C(44)–N(45)–Ru(2)	169.6(5)
Ru(1)–P(25)	2.330(2)	C(50)–N(49)–Ru(2)	171.6(5)
Ru(2)–N(45)	2.021(5)	P(25)–Ru(1)–P(6)	100.23(6)
Ru(2)–N(49)	2.007(5)	N(49)–Ru(2)–N(45)	174.3(2)
Ru(2)–P(94)	2.292(2)	N(49)–Ru(2)–O(48)	88.6(2)
Ru(2)–O(48)	2.215(5)	N(45)–Ru(2)–O(48)	85.8(2)
Ru(2)–Cl(47)	2.327(2)	N(49)–Ru(2)–P(94)	93.5(2)
Ru(2)–Cl(46)	2.348(2)	N(45)–Ru(2)–P(94)	92.1(2)
Ru(3)–C(50)	1.974(7)	O(48)–Ru(2)–P(94)	177.4(1)
Ru(3)–Ct(2)	1.887(7)	N(49)–Ru(2)–Cl(47)	89.0(2)
Ru(3)–P(56)	2.312(2)	N(45)–Ru(2)–Cl(47)	89.3(2)
Ru(3)–P(75)	2.336(2)	O(48)–Ru(2)–Cl(47)	84.5(1)
C(44)–N(45)	1.159(8)	P(94)–Ru(2)–Cl(47)	93.89(6)
C(50)–N(49)	1.166(8)	N(49)–Ru(2)–Cl(46)	88.6(2)
		N(45)–Ru(2)–Cl(46)	92.2(2)
		O(48)–Ru(2)–Cl(46)	87.2(1)
		P(94)–Ru(2)–Cl(46)	94.51(6)
		Cl(47)–Ru(2)–Cl(46)	171.39(6)
		P(56)–Ru(3)–P(75)	99.30(6)
		H(48A)–O(48)–H(48B)	99.49(14)

Conclusions

We have prepared and fully characterized the new organometallic trinuclear ruthenium aqua complex $[\{(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru(\mu\text{-}CN)\}_2RuCl_2(PPh_3)(H_2O)]PF_6$ and isolated it in moderate yield by using a relatively simple synthetic strategy and trivial starting materials. The structure of the complex was determined by X-ray diffraction, confirming the structural assignments obtained from the spectroscopic data. The isolated organometallic trinuclear aqua compound represents one of the few examples of a Ru–C≡**N**–Ru′–**N**≡C–Ru array with a metal–metal interaction across the cyanide bridges and probably over more than one CN linkage. Because of the steric strain imposed by the large PPh_3 ligand at the central ruthenium, the complex shows a marked deviation from the expected linearity of the Ru–C≡**N**–Ru′–**N**≡C–Ru array. The lability of the aqua ligand can lead to a convenient synthetic route for the preparation of other tri- and tetranuclear cyanide-bridged complexes. Further studies on this organometallic trinuclear ruthenium aqua complex are in progress in order to explore fundamental properties such as its reactivity in selected transformations, for example in ring-opening metathesis polymerization (ROMP).

Experimental Section

General: All the experiments were carried out under vacuum or a nitrogen atmosphere by use of standard vacuum line Schlenk-tube techniques. All the solvents used were distilled and dried according to the usual published methods.[19] The compounds [(η^5-C_5H_5)$(PPh_3)_2RuCN$][5,20] (**2**) and [$RuCl_2(PPh_3)_3$][21] (**3**) were prepared following methods described in the literature, and the spectroscopic data (UV/Vis and/or NMR) agreed with that reported. The UV/Vis spectra were recorded with a GBC-Cintra 40 UV/Vis spectrometer using 1 cm optical path quartz cells with freshly prepared solutions (ca. 2×10^{-4} M) in dichloromethane (dcm), chloroform, and dimethylformamide (dmf). The spectrum is presented as λ_{max} or shoulder (sh.) [nm] (ε_{max} [$M^{-1}cm^{-1}$]). The mass spectra (TOF-MS) were recorded with a Micromass LCT; peaks are reported as *m/z* (assignment, relative intensity). IR spectra were recorded by using a Nicolet Avatar 360 FTIR spectrometer, calibrated with polystyrene, with KBr pellets; only significant bands are cited in the text. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker AM500 spectrometer at 500.13 MHz (^1H), 125.76 MHz (^{13}C), and 202.46 MHz (^{31}P); probe temperature (30 °C) in $CDCl_3$. The ^1H chemical shifts (δ), reported in parts per million (ppm) downfield, are referenced to residual chloroform (δ = 7.24 ppm). The $^{13}C\{^1H\}$ chemical shifts are reported in ppm relative to the carbon resonance of the deuterated NMR solvent: $CDCl_3$ (δ = 77.00 ppm). The $^{31}P\{^1H\}$ NMR spectra are reported in ppm downfield from the external standard 85% H_3PO_4 at δ = 0.00 ppm. Melting points were obtained on a Leica Gallen instrument and were not corrected.

Preparation of [{(η^5-C_5H_5)$(PPh_3)_2Ru(\mu$-CN)}$_2RuCl_2(PPh_3)(H_2O)$]PF_6 (1): To a mixture of [(η^5-C_5H_5)$(PPh_3)_2RuCN$] (0.100 g, 0.14 mmol) and [$RuCl_2(PPh_3)_3$] (0.138 g, 0.14 mmol) in THF (30 mL) was added NH_4PF_6 (0.114 g, 0.7 mmol). The mixture was stirred at 60 °C for 3 h, then at 20 °C for 22 h. The color of the reaction mixture changed slowly from black-red to dark (almost black) green-blue. The solution was evaporated to dryness in vacuo. Dichloromethane (10 mL) was then added. The precipitate of ammonium salts was removed by cannula filtration, and the filtrate was evaporated to dryness and dried in vacuo. The resulting dark green-blue solid was recrystallized from a mixture of *n*-pentane/dichloromethane/diethyl ether (3 mL/6 mL/0.5 mL) to obtain dark blue crystals. Yield: 85 mg (59%). M.p. 184–187 °C. FTIR (KBr): υ_{OH} 3056 (br.), υ_{CN} 2052 (m), δ_{OH} 1635 (br.), υ_{PF6} 841 (s), 520 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.57–7.30 (m, 75 H, Ph), 5.30 (s, 10 H, C_5H_5), 3.73 (s, H_2O) ppm. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 146.7 (CN), 133.6–127.3 (Ph) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ = 30.0 (s, 4 P, PPh_3), 17.8 (s, 1 P, PPh_3), –143.7 (m, PF_6) ppm. $C_{102}H_{87}Cl_2F_6N_2OP_6Ru_3$ (2030.74): calcd. C 60.3, H 4.3, N 1.4; found C 59.7, H 4.4, N 1.6. TOF-MS (ES^+): *m/z* (%) = calcd. 429.0, found 429.2 (84) [(η^5-C_5H_5)$Ru(PPh_3)$]$^+$; calcd. 626.1, found 625.4 (100) [$Ru(PPh_3)_2$]$^+$; calcd. 1151.1, found 1151.7 (50) [(η^5-C_5H_5)$(PPh_3)_2Ru(\mu$-CN)$RuCl_2(PPh_3)$]$^+$; calcd. 1868.2, found 1868.2 (75) [M – PF_6 – H_2O]$^+$; calcd. 1886.2, found 1886.2 (10) [M – PF_6]$^+$. UV/Vis (CH_2Cl_2): λ_{max} (ε_{max}, $M^{-1}cm^{-1}$) = 658 (3937).

Single Crystal X-ray Diffraction: Data were recorded with a Nonius Kappa Apex II diffractometer by using graphite monochromatized Mo-K_α radiation [λ(Mo-K_α) = 0.71073 Å] and a temperature of 173.0 ± 0.1 K. The data were processed with Denzo-SMN v0.97.638.[22] The structure was solved by direct methods (SHELXS-97),[23] and refinements based on F^2 were made by full-matrix least-squares techniques (SHELXL-97).[24] Graphics program ORTEP3 for Windows[18] was executed through the WinGX-suite.[25] The hydrogen atoms were calculated to their idealized positions with isotropic temperature factors (1.2 or 1.5 times the C temperature factor) and as riding atoms. The water hydrogen atoms were located from the difference Fourier map, but refined as riding atoms with isotropic temperature factors 1.5 times the O temperature factor.

In the structure, only one of the approximately 3.5 dichloromethane (dcm) molecules was found to be non-disordered and was refined with full occupancy, one full dcm molecule was disordered over four sites, and one dcm molecule was refined with a one third occupancy. Residual electron density showed high peaks, which could not be modeled with any chemically reasonable model (they probably arise because of severely disordered dcm molecules) and were treated as Cl atoms with partial occupancy.

CCDC-626456 for **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting information (see footnote on the first page of this article): The cyclic voltammogram and van der Waals and ball-and-stick representations of compound **1** are available.

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[1] A search in the SciFinder 2006 retrieved 860 references for the keyword "cyanide-bridged".

[2] The number of di/trinuclear structures found in a Cambridge Structural Database (CSD) [CSD version 5.27 (August-2006 update)] search revealed 2091 hits for the dinuclear complexes of general formula M–CN–M, but only 932 hits for the trinuclear compounds of general formula M–CN–M′–NC–M.

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