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Synthesis and Structure of Binuclear Chromium(III) Complexes with Unfolded Diamine Schiff Bases of 1,3,5-Triketones. Molecular Structure of Tris[7,7′-(1,2-ethanediyldinitrilo)bis(2,2-dimethyl-3,5-octanedionato)(2–)]dichromium(III)-6-Pyridine-1-Water, $Cr_2[(HPAA)_2en]_3·6py·H_2O$

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Binuclear Cr(III) complexes of the diamine Schiff-base derivatives of 1,3,5-triketones have been synthesized. The stoichiometry of the products is Cr_2L_3 where L is the dianion of the Schiff-base ligand. These compounds represent the first completely characterized binuclear complexes of trivalent metal ions with this class of ligands. Crystallization from pyridine yields crystals of the title compound suitable for X-ray structure determination. The red-brown crystals are monoclinic, space group $P2_1n$, with 4 molecules per unit cell. The lattice constants are a = 15.113 (2) Å, b = 22.899 (2) Å, c = 29.184 (3) Å, β = 92.90°, and V = 10 087 (2) Å^3. The molecule consists of three unfolded ligands in which the 1,3-diketone ends of each are bound to two different Cr(III) ions. The coordination environment of each chromium is pseudooctahedral with six enolate oxygens. The chromium atoms are 10.3 Å apart.

Introduction

Condensation of diamines with 1,3,5-triketones in which the 5-substituent is phenyl or *tert*-butyl and the 1-substituent is CH_3 results in ligands capable of binding two metal ions in different coordination environments. A synthetic strategy was developed in our laboratory that made use of such ligands to preferentially bind two different metal ions in the same molecule in a manner that ensured that only one positional isomer resulted.[1] This general method has been employed by other groups with the same ligands and, at times, in preparation of the same compounds[2] and with other related ligands.[3-5] Our early studies dealt with developing the synthetic approach[1] and with the structural characterization of enough heterobinuclear products to clearly illustrate the potential of the approach and the general ligand system.[1,6-8] The same procedures were employed to prepare the mixed-spin-state binuclear Ni(II) complex in which the N_2O_2-coordinated Ni(II) is square planar low spin while the O_2O_2-coordinated Ni(II) is octahedral high spin through the binding of two solvent molecules.[9]

While the general utility of the binucleating diamine Schiff-base ligands has been demonstrated for divalent metal ion, no systematic attempts have been reported for the preparation and characterization of trivalent complexes. This study was undertaken as our initial attempt to investigate such binuclear complexes.

Experimental Section

Ligand Synthesis. The triketone, 2,2-dimethyl-3,5,7-octanetrione, H_2PAA, was prepared by the method of Miles, Harris, and Hauser.[10] The Schiff-base derivatives with ethylenediamine, $(H_2PAA)_2en$, and 1,3-propanediamine, $(H_2PAA)_2$-1,3-pn, were prepared by the condensation of H_2PAA with a small excess (5%) of the appropriate diamine in absolute methanol. Systematic names for $(H_2PAA)_2en$ and $(H_2PAA)_2$-1,3-pn are 7,7′-(1,2-ethanediylnitrilo)bis(2,2-dimethyl-3,5-octanedione) and 7,7′-(1,3-propanediyldinitrilo)bis(2,2-dimethyl-3,5-octanedione).

Table I. X-ray Experimental Data for $Cr_2[(HPAA)_2en]_3·6py·H_2O$

formula	$Cr_2C_{96}H_{134}N_{12}O_{13}$
mol wt	1766
color	red-brown
radiation used	Mo Kα (0.710 688 Å)
cryst syst	monoclinic
space gp	$P2_1n$
ρ, g cm^{-3}	1.164
a, Å	15.113 (2)
b, Å	22.899 (2)
c, Å	29.184 (3)
β, deg	92.90 (1)
V, Å^3	10087 (2)
Z	4
type of scan	$\theta/2\theta$
scan range, deg	$K_{\alpha_1\text{-}1}-K_{\alpha_2\text{-}2}$
scan rate, deg/min	fixed at 2
bkgd as a function of scan time	0.50
collecn region	$+h,+k,\pm l$
2θ limits, deg	2–45
no. of data collecd	14 796
max dev of stds during collecn	~5%
cor applied	LP and decay
data with $F_o^2 \geq 3\sigma(F_o^2)$	4462
no. of variables	355
μ, cm^{-1}	2.69
cor made?	no
soln method	F^2 Patterson
H atoms located?	calcd
bond dist, Å	0.95
temp factor	$B_H = 1.10B_C$ or $\text{-}B_N$
refinement method	full-matrix least squares
weights	$[1/\sigma(F_o)]^2$
quantity min	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Cr atoms	anisotropic
other non-H atom	isotropic
H atoms	fixed
R_1[a]	0.094
R_2[b]	0.114
S[c]	2.634
resid electron density, e/Å^3	0.534
scattering factors	11, 12, 13

[a] $R_1 = \sum[\lvert F_o\rvert - \lvert F_c\rvert]/\sum\lvert F_o\rvert$. [b] $R_2 = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$. [c] $S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variable parameters.

Synthesis of $Cr_2[(HPAA)_2en]_3$ and $Cr_2[(HPAA)_2$-1,3-pn$]_3$. A solution of 1.28 × 10^{-3} *m* of the ligand dissolved in 130 mL of CH_3OH was placed in a flask fitted with a Soxhlet extractor and condensor. A thimble containing 0.257 g (1.37 × 10^{-3} *m*) of $Cr(C_2H_3O_2)_2·H_2O$ was placed in

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0020-1669/85/1324-1819$01.50/0

Table II. Final Positional and Thermal Parameters for $Cr_2[(HPAA)_2en]_3{\cdot}6py{\cdot}H_2O^a$

atom	*x*	*y*	*z*	B_{iso}, Å^2	atom	*x*	*y*	*z*	B_{iso}, Å^2
Cr(1)	−0.0392 (1)	0.0144 (1)	0.1727 (1)		C(24)	0.0026 (12)	0.0179 (8)	0.3584 (6)	8.8 (5)
Cr(2)	0.2230 (1)	0.3331 (1)	0.0164 (1)		C(25)	0.0785 (12)	−0.0558 (8)	0.3133 (6)	8.6 (5)
O(1)	−0.1614 (6)	0.0133 (4)	0.1887 (3)	4.7 (2)	C(26)	−0.0062 (10)	−0.0178 (6)	0.3146 (5)	5.0 (3)
O(2)	−0.0743 (6)	0.0428 (4)	0.1103 (3)	4.0 (2)	C(27)	−0.0096 (9)	0.0193 (6)	0.2701 (5)	4.2 (3)
O(3)	0.2588 (6)	0.2512 (4)	0.0108 (3)	3.9 (2)	C(23)	−0.0209 (9)	0.0795 (6)	0.2723 (5)	4.4 (3)
O(4)	0.3470 (6)	0.3554 (4)	0.0248 (3)	4.1 (2)	C(29)	−0.0248 (8)	0.1162 (6)	0.2335 (5)	4.0 (3)
O(5)	−0.0042 (5)	−0.0115 (4)	0.2345 (3)	4.1 (2)	C(30)	−0.0243 (9)	0.1777 (7)	0.2412 (5)	5.0 (4)
O(6)	−0.0239 (5)	0.0961 (4)	0.1922 (3)	3.9 (2)	C(31)	−0.0269 (10)	0.2188 (7)	0.2061 (6)	5.1 (4)
O(7)	0.0988 (6)	0.3081 (4)	0.0058 (3)	4.0 (2)	C(32)	−0.0324 (11)	0.2819 (7)	0.2215 (6)	7.5 (5)
O(8)	0.2295 (6)	0.3455 (4)	−0.0489 (3)	4.4 (2)	C(33)	−0.0289 (11)	0.2488 (8)	0.1263 (6)	7.6 (5)
O(9)	−0.0497 (6)	−0.0671 (4)	0.1534 (3)	4.3 (2)	C(34)	−0.0646 (12)	0.2254 (8)	0.0849 (7)	7.8 (5)
O(10)	0.0846 (6)	0.0138 (4)	0.1546 (3)	4.2 (2)	C(35)	−0.1787 (12)	0.2577 (7)	0.0036 (6)	7.3 (5)
O(11)	0.2131 (5)	0.3212 (4)	0.0827 (3)	3.9 (2)	C(36)	−0.0817 (10)	0.2734 (6)	0.0065 (5)	4.9 (4)
O(12)	0.1889 (5)	0.4148 (4)	0.0244 (3)	4.2 (2)	C(37)	−0.0434 (10)	0.3009 (6)	−0.0289 (5)	4.9 (4)
N(1)	−0.0123 (9)	0.0785 (5)	0.0326 (4)	6.4 (3)	C(38)	0.0473 (9)	0.3178 (5)	−0.0293 (5)	3.6 (3)
N(2)	0.2043 (9)	0.1413 (6)	0.0087 (4)	6.6 (3)	C(39)	0.0782 (9)	0.3422 (6)	−0.0709 (5)	4.8 (4)
N(3)	−0.0325 (8)	0.2067 (5)	0.1637 (4)	5.4 (3)	C(40)	0.1663 (10)	0.3534 (6)	−0.0781 (5)	4.4 (3)
N(4)	−0.0352 (8)	0.2585 (5)	0.0444 (4)	5.9 (3)	C(41)	0.1945 (12)	0.3749 (8)	−0.1254 (6)	7.0 (4)
N(5)	0.2223 (8)	0.0811 (5)	0.1426 (4)	5.4 (3)	C(42)	0.2344 (15)	0.4337 (10)	−0.1176 (8)	11.7 (7)
N(6)	0.2124 (8)	0.2411 (5)	0.1492 (4)	5.3 (3)	C(43)	0.1233 (15)	0.3752 (10)	−0.1616 (8)	11.7 (7)
C(1)	−0.3024 (12)	−0.0719 (8)	0.1965 (6)	8.7 (5)	C(44)	0.2631 (15)	0.3358 (10)	−0.1402 (7)	11.7 (7)
C(2)	−0.3258 (13)	0.0284 (8)	0.2253 (7)	9.6 (6)	C(45)	−0.0688 (11)	−0.1751 (7)	0.1946 (6)	7.3 (5)
C(3)	−0.3972 (14)	−0.0030 (8)	0.1515 (7)	9.7 (6)	C(46)	0.0540 (13)	−0.2111 (8)	0.1515 (6)	8.7 (5)
C(4)	−0.3144 (10)	−0.0086 (7)	0.1828 (5)	5.5 (4)	C(47)	−0.0853 (12)	−0.1771 (8)	0.1120 (6)	8.3 (5)
C(5)	−0.2293 (9)	0.0127 (6)	0.1606 (5)	4.2 (3)	C(48)	−0.0182 (10)	−0.1664 (7)	0.1519 (5)	5.1 (4)
C(6)	−0.2291 (9)	0.0262 (6)	0.1141 (5)	4.5 (3)	C(49)	0.0129 (9)	−0.1031 (6)	0.1532 (4)	3.6 (3)
C(7)	−0.1526 (9)	0.0429 (5)	0.0910 (5)	3.7 (3)	C(50)	0.0987 (10)	−0.0894 (6)	0.1520 (5)	4.6 (3)
C(8)	−0.1633 (9)	0.0595 (6)	0.0443 (5)	4.4 (3)	C(51)	0.1343 (9)	−0.0313 (6)	0.1500 (4)	4.1 (3)
C(9)	−0.0976 (11)	0.0760 (6)	0.0169 (5)	5.2 (4)	C(52)	0.2257 (10)	−0.0216 (7)	0.1420 (5)	5.4 (4)
C(10)	−0.1204 (12)	0.0923 (8)	−0.0324 (7)	8.9 (5)	C(53)	0.2661 (11)	0.0311 (7)	0.1381 (5)	5.8 (4)
C(11)	0.0556 (16)	0.1086 (10)	0.0060 (8)	11.2 (6)	C(54)	0.3622 (12)	0.0357 (7)	0.1310 (6)	7.5 (5)
C(12)	0.1399 (15)	0.0976 (9)	0.0265 (7)	10.3 (6)	C(55)	0.2561 (11)	0.1407 (8)	0.1409 (6)	7.1 (4)
C(13)	0.3084 (13)	0.0673 (9)	−0.0112 (7)	9.7 (6)	C(56)	0.1971 (11)	0.1802 (8)	0.1609 (6)	6.9 (4)
C(14)	0.2858 (12)	0.1301 (7)	−0.0027 (5)	6.5 (4)	C(57)	0.2191 (11)	0.2742 (7)	0.2277 (6)	7.7 (5)
C(15)	0.3497 (9)	0.1728 (7)	−0.0091 (5)	4.6 (3)	C(58)	0.2165 (9)	0.2870 (7)	0.1760 (5)	4.9 (4)
C(16)	0.3349 (9)	0.2329 (6)	−0.0004 (4)	3.8 (3)	C(59)	0.2213 (9)	0.3433 (6)	0.1614 (5)	4.9 (4)
C(17)	0.4109 (9)	0.2701 (6)	−0.0025 (4)	3.7 (3)	C(60)	0.2177 (9)	0.3598 (6)	0.1144 (5)	4.0 (3)
C(18)	0.4120 (8)	0.3259 (6)	0.0105 (4)	3.3 (3)	C(61)	0.2167 (9)	0.4211 (6)	0.1034 (5)	4.1 (3)
C(19)	0.4952 (9)	0.3637 (6)	0.0086 (5)	4.4 (3)	C(62)	0.2011 (8)	0.4440 (6)	0.0609 (5)	3.7 (3)
C(20)	0.4818 (12)	0.4071 (8)	−0.0289 (7)	9.5 (6)	C(63)	0.1923 (11)	0.5106 (7)	0.0534 (6)	6.0 (4)
C(21)	0.5088 (12)	0.3961 (8)	0.0537 (7)	9.2 (5)	C(64)	0.1007 (13)	0.5224 (8)	0.0334 (6)	9.3 (5)
C(22)	0.5801 (13)	0.3286 (8)	0.0011 (7)	9.5 (6)	C(65)	0.i557 (14)	0.5266 (9)	0.0186 (7)	10.3 (6)
C(23)	−0.0879 (12)	−0.0556 (8)	0.3138 (6)	8.4 (5)	C(66)	0.2119 (16)	0.5453 (11)	0.0947 (9)	13.3 (8)

[a] The standard deviations in parentheses refer to the least significant digits.

the extractor. The flask was heated to reflux and refluxed for 12 h. During this time an olive green solid formed in the flask. The solid was recovery, washed with H_2O and CH_3OH, and air-dried. Anal. Calcd for $Cr_2[(HPAA)_2en]_3$, $C_{66}H_{102}O_{12}N_6Cr_2$: C, 62.15; H, 8.06; N, 6.59; Cr, 8.15. Found: C, 61.43; H, 7.74; N, 6.40; Cr, 8.41. Anal. Calcd for $Cr_2[(HPAA)_2$-1,3-pn$]_3$, $C_{69}H_{108}O_{12}N_6Cr_2$: C, 62.90; H, 8.26; N, 6.38; Cr, 7.89. Found: C, 62.73; H, 8.42; N, 6.33; Cr, 7.88.

Crystallization of $Cr_2[(HPAA)_2en]_3$ from pyridine yields reddish brown rectangular crystals suitable for X-ray analysis. Elemental analysis indicates a formula $Cr_2[(HPAA)_2en]_3{\cdot}6py$. Anal. Calcd for $Cr_2[(HPAA)_2en]_3{\cdot}6py$, $C_{96}H_{132}O_{12}N_{12}Cr_2$: C, 65.90; H, 7.55; N, 9.61; Cr, 5.95. Found: C, 65.72; H, 7.54; N, 9.40; Cr, 6.11. Crystallization of $Cr_2[(HPAA)_2$-1,3-pn$]_3$ from pyridine also yields a crystalline product in the form of dark green needles. Elemental analysis was not performed on this product. These crystals lose pyridine at about 80 °C but do not melt until 300 °C.

Spectroscopy. Infrared spectra were recorded with a Perkin-Elmer 283B double-beam spectrometer in KBr pellets. The UV-visible spectra were recorded on a Perkin-Elmer Lambda 3 spectrophotometer equipped with a Model 3600 Data Station. Spectrograde CCl_4 was used as the solvent.

Crystallography and Structure Determination. A suitable red-brown crystal of $Cr_2[(HPAA)_2en]_3{\cdot}6py{\cdot}H_2O$ was mounted on a glass fiber with epoxy cement, covered with silicon grease to prevent evaporation of solvate molecules, and placed on a Syntex $P2_1$ four-circle diffractometer. Pertinent information regarding data collection, structure solution, and refinement of procedures may be found in Table I. Positional and thermal parameters are in Table II. Bond distances and angles are in Tables III and IV. The labeling scheme for the atoms is shown in Figure 1. Tables of hydrogen and solvate atom positional and thermal parameters, observed and calculated structure factors, and anisotropic thermal parameters for the chromium atoms have been deposited as supplementary material.

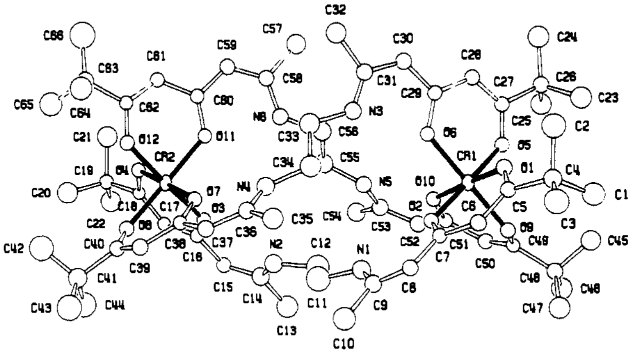

Figure 1. Atom-numbering scheme for $Cr_2[(HPAA)_2en]_3$.

Results and Discussion

The crystallization of $Cr_2[(HPAA)_2en]_3$, an olive green powder, from pyridine results in red-brown rectangular crystals that differ from the starting material by the addition of six pyridines and one water of solvation. This unusual molecule consists of three unfolded Schiff-base ligands, $(HPAA)_2en^{2-}$, in which the two 1,3-diketonate moieties in each ligand are bound to two different Cr(III) ions. An ORTEP diagram of the complex is shown in Figure 2. This is in marked contrast to the more normal bonding mode observed with divalent metal ions shown in Figure 3. The ORTEP

Table III. Bond Lengths (Å) for the Complex $Cr_2[(HPAA)_2en]_3 \cdot 6py \cdot H_2O$

	Chromium–Oxygen Bonds		
Cr(1)–O(1)	1.927 (9)	Cr(2)–O(3)	1.961 (9)
Cr(1)–O(2)	1.981 (8)	Cr(2)–O(4)	1.946 (9)
Cr(1)–O(5)	1.947 (9)	Cr(2)–O(7)	1.972 (9)
Cr(1)–O(6)	1.967 (9)	Cr(2)–O(8)	1.932 (9)
Cr(1)–O(9)	1.952 (9)	Cr(2)–O(11)	1.966 (9)
Cr(1)–O(10)	1.970 (9)	Cr(2)–O(12)	1.960 (9)
	Ring C–C and C–O Bonds		
O(5)–C(27)	1.26 (2)	O(3)–C(16)	1.28 (2)
C(27)–C(28)	1.39 (2)	C(16)–C(17)	1.43 (2)
C(28)–C(29)	1.41 (2)	C(17)–C(18)	1.33 (2)
C(29)–O(6)	1.29 (2)	C(18)–O(4)	1.28 (2)
O(1)–C(5)	1.28 (2)	O(11)–C(60)	1.28 (2)
C(5)–C(6)	1.39 (2)	C(60)–C(61)	1.44 (2)
C(6)–C(7)	1.42 (2)	C(61)–C(62)	1.36 (2)
C(7)–O(2)	1.29 (2)	C(62)–O(12)	1.26 (2)
O(9)–C(49)	1.26 (2)	O(7)–C(38)	1.27 (2)
C(49)–C(50)	1.34 (2)	C(38)–C(39)	1.44 (2)
C(50)–C(51)	1.44 (2)	C(39)–C(40)	1.38 (2)
C(51)–O(10)	1.29 (2)	C(40)–O(8)	1.26 (2)
	Imine Bonds		
N(1)–C(9)	1.35 (2)	N(4)–C(36)	1.32 (2)
N(2)–C(14)	1.32 (2)	N(5)–C(53)	1.33 (2)
N(3)–C(31)	1.27 (2)	N(6)–C(58)	1.31 (2)

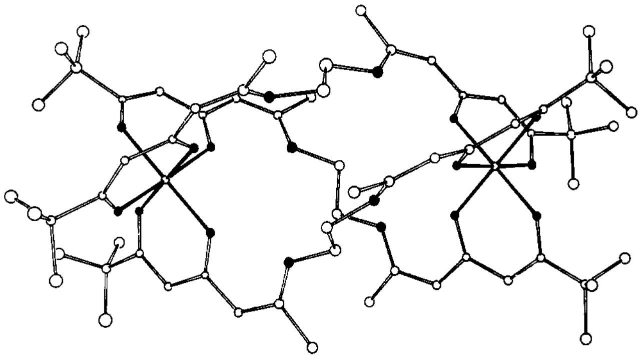

Figure 2. ORTEP drawing of $Cr_2[(HPAA)_2en]_3 \cdot 6py \cdot H_2O$.

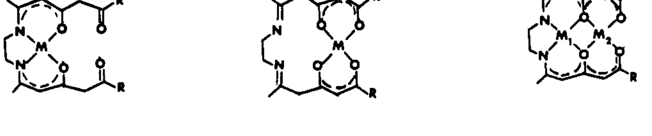

Figure 3. "Normal" bonding modes for Schiff-base triketonate complexes.[1,6,8]

drawing in Figure 2 clearly shows that the ligands describe a left-handed helix (Λ) with both chromium atoms, coordinated in typical six-coordinate fashion, adopting a Λ absolute configuration. The chromium atoms in these molecules are 10.3 Å apart. This distance seems incredibly long for formation of a discrete molecular species. Since there are clear possibilities for polymer formation, it is surprising that all three of the initially complexed, unfolded ligands on the first chromium atom have found their way to the same second chromium atom, especially when the distances are so long.

The infrared spectrum of $Cr_2[(HPAA)_2\text{-}1,3\text{-}pn]_3$ leaves little doubt that it has the same basic structure as that of $Cr_2[(HPAA)_2en]_3$ (Figure 4 (supplementary material)). The spectra of the two are virtually identical, except for some intensity differences and two additional bands at about 1300 and 1100 cm^{-1} in the 1,3-pn derivative. Thus, this unusual mode of bonding persists even when the three chains linking the coordination spheres are increased by one CH_2 unit from eight atoms to nine. The UV–visible spectra are also very similar to the two compounds.

Table IV. Angles (deg) for the Complex $Cr_2[(HPAA)_2en]_3 \cdot 6py \cdot H_2O$

	Coordination Sphere Angles		
O(1)–Cr(1)–O(2)	90.7 (4)	O(3)–Cr(2)–O(4)	89.6 (4)
O(1)–Cr(1)–O(5)	89.5 (4)	O(3)–Cr(2)–O(7)	88.5 (4)
O(1)–Cr(1)–O(6)	92.4 (4)	O(3)–Cr(2)–O(8)	91.8 (4)
O(1)–Cr(1)–O(9)	89.6 (4)	O(3)–Cr(2)–O(11)	89.1 (4)
O(1)Cr(1)–O(10)	178.1 (6)	O(3)–Cr(2)–O(12)	177.8 (4)
O(2)–Cr(1)–O(5)	178.5 (6)	O(4)–Cr(2)–O(7)	177.5 (4)
O(2)–Cr(1)–O(6)	88.6 (3)	O(4)–Cr(2)–O(8)	89.4 (4)
O(2)–Cr(1)–O(9)	92.0 (3)	O(4)–Cr(2)–O(11)	91.9 (3)
O(2)–Cr(1)–O(10)	88.3 (4)	O(4)–Cr(2)–O(12)	89.5 (4)
O(5)–Cr(1)–O(6)	89.9 (4)	O(7)–Cr(2)–O(8)	89.1 (4)
O(5)–Cr(1)–O(9)	89.4 (4)	O(7)–Cr(2)–O(11)	89.7 (4)
O(5)–Cr(1)–O(10)	91.6 (4)	O(7)–Cr(2)–O(12)	92.4 (4)
O(6)–Cr(1)–O(9)	177.9 (6)	O(8)–Cr(2)–O(11)	178.5 (5)
O(6)–Cr(1)–O(10)	89.1 (4)	O(8)–Cr(2)–O(12)	90.3 (4)
O(9)–Cr(1)–O(10)	88.9 (4)	O(11)–Cr(2)–O(12)	88.9 (4)
	Ring Angles		
O(5)–C(27)–C(28)	127 (1)	O(3)–C(16)–C(17)	123 (1)
C(27)–C(28)–C(29)	124 (1)	C(16)–C(17)–C(18)	124 (1)
C(28)–C(29)–O(6)	122 (1)	C(17)–C(18)–O(4)	127 (1)
O(1)–C(5)–C(6)	125 (1)	O(11)–C(60)–C(61)	121 (1)
C(5)–C(6)–C(7)	124 (1)	C(60)–C(61)–C(62)	126 (1)
C(6)–C(7)–O(2)	123 (1)	C(61)–C(62)–O(12)	125 (1)
O(9)–C(49)–C(50)	125 (1)	O(7)–C(38)–C(39)	122 (1)
C(49)–C(50)–C(51)	126 (1)	C(38)–C(39)–C(40)	124 (1)
C(50)–C(51)–O(10)	121 (1)	C(39)–C(40)–O(8)	125 (1)
	Angles around Imines		
C(8)–C(9)–C(10)	119 (1)	C(37)–C(36)–C(35)	121 (1)
C(8)–C(9)–N(1)	122 (1)	C(37)–C(36)–N(4)	122 (1)
C(10)–C(9)–N(1)	119 (1)	C(35)–C(36)–N(4)	117 (1)
C(15)–C(14)–C(13)	119 (2)	C(52)C(53)–C(54)	122 (1)
C(15)–C(14)–N(2)	124 (2)	C(52)–C(53)–N(5)	122 (1)
C(13)–C(14)–N(2)	117 (2)	C(54)–C(53)–N(5)	117 (1)
C(30)–C(31)–C(32)	115 (1)	C(59)–C(58)–C(57)	119 (1)
C(30)–C(31)–N(3)	125 (1)	C(59)–C(58)–N(6)	125 (1)
C(32)–C(31)–N(3)	120 (1)	C(57)–C(58)–N(6)	116 (1)

Table V. UV–Visible Spectra of the Binuclear Cr(III) Complexes

	λ_{max}, cm^{-1} (ϵ, L mol^{-1} cm^{-1})	
transition	$Cr_2[(HPAA)_2en]_3$	$Cr_2[(HPAA)_2]\text{-}1,3\text{-}pn]_3$
$^4T_{2g} \rightarrow {}^4A_{2g}$	17 610 (140)	17 500 (350)
$^4T_{1g} \rightarrow {}^1A_{2g}$	20 530 (668)	20 650 (960)
L → M	25 130 (50 060)	25 570 (57 425)
L → M	26 160 (81 590)	26 340 (64 595)
$\pi^* \rightarrow \pi$	31 740 (18 532)	31 840 (16 430)

They exhibit two d–d bands, two bands that are most likely charge-transfer transitions, and one intraligand band. The energies and molar extinction coefficients for these bands obtained in CCl_4 are given in Table V. These energies are very similar to those observed for the analogous diketonate, tris(2,2-dimethyl-1,3-pentanedionato)chromium(III), complex:[14] 17 860, 23 590, 25 770, 29 240, and 32 470 cm^{-1}.

An intriguing aspect of these molecules is that their centers consist of a reasonably open space surrounded by six protonated imine-type nitrogens and six oxygens. Each of these atoms is a potential electron pair donor, which opens the possibility of binding one or more additional metal ions to these molecules in an encapsulating manner.

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Registry No. $Cr_2[(HPAA)_2en]_3$, 95978-23-7; $Cr_2[(HPAA)_2en]_3 \cdot 6py \cdot H_2O$, 95998-60-0; $Cr_2[(HPAA)_2\text{-}1,3\text{-}pn]_3$, 95978-24-8.

Supplementary Material Available: Figure 4 showing IR spectra and complete listings of final positional and thermal parameters, observed and calculated structure factors, and anisotropic thermal parameters (27 pages). Ordering information is given on any current masthead page.

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[14] Fatta, A. M.; Lintvedt, R. L. *Inorg. Chem.* **1971**, *10*, 478.