added KCl facilitates formation of the dimer.[19]

No spectral changes occur when H_2TPPS^{4-} is treated with $N_8H_4^{4+}$ (pH ~ $8.5^{2,3}$) nor when H_4TPPS^{2-} is mixed with the smaller macrocycle 1,4,7,10,13,16-hexaazacyclooctadecane in the tetraprotonated form (pH ~ 3.5^{20}). There is no spectral interaction between $N_8H_8^{8+}$ and H_2TMPyP^{4+}(tetrakis(*N*-methylpyrid-4-yl)porphine cation), but H_2TPPC^{4-} **2b**, R = CO_2^-(tetrakis(4-carboxyphenyl)porphine anion),[19,21] gives similar spectral changes to that of H_2TPPS^{4-} when treated with $N_8H_8^{8+}$. It has been found that the chemical reactivity and photochemical properties of $TPPS^{4-}$ and metalloderivatives[22-24] are markedly modified in the amine-induced dimer. These are manifest in, for example, reduced rates of interaction of the porphyrin with metal ions and in the loss of the relatively long lifetime of the first excited triplet.[24] These studies are continuing.

Acknowledgment. This work was supported by a National Science Foundation grant (CHE-8613217) which is gratefully acknowledged.

Supplementary Material Available: Spectral titration of H_2TPPS^{4-} by $N_8H_8^{8+}$ at 25 °C and a table of spectral characteristics of H_2TPPS^{4-}, H_4TPPS^{2-}, and metalloderivatives and their adducts with $N_8H_8^{8+}$ (2 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of $Cp_3Co_3(CO)_2$

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An extensive series of triangular clusters having the general form $(CpM)_3(CO)_2$ is known which exhibits a variety of interesting structural and spectroscopic properties.[1] The formal valence electron count for these neutral clusters may be varied from 46 (M = Co) to 49 (M = Ni). The lower electron count clusters appear to be stabilized by electron-rich ligands such as pentamethylcyclopentadiene (Cp*) as opposed to cyclopentadiene (Cp). We have recently developed a synthetic route into more reactive $46e^-$ clusters which contain at least one Cp ligand.[2] Here we describe the synthesis, structure, magnetic properties, and surprising reactivity of $(CpCo)_3(CO)_2$, **1**.

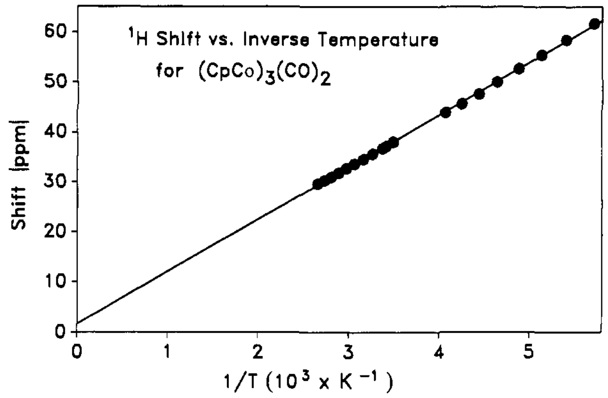
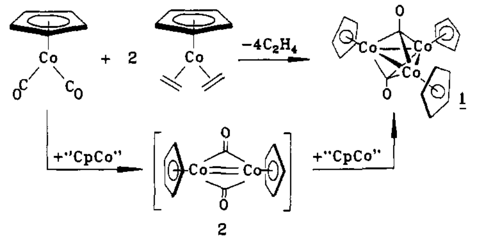


Figure 1. Paramagnetically induced temperature dependence of the ^{1}H NMR spectrum of **1**. The diamagnetic reference position for the Cp ring protons of **1** was assumed to be 5 ppm. The paramagnetic shift is defined according to the following equation: $\delta_{obsd} = \delta_{dia} + \delta_{para}$.

Scheme I



Although the title complex is quite oxygen sensitive and spontaneously decomposes when dissolved in all organic solvents investigated thus far, it may be conveniently synthesized by the reaction of $CpCo(C_2H_4)_2$ and $CpCo(CO)_2$ as summarized in Scheme I.

The reaction must be conducted by using hexane as the major solvent to cause the trinuclear complex to precipitate as it is formed. In this way, yields of **1** as high as 70% may be obtained. The formation of the trinuclear product occurs in a stepwise manner involving formation of the known dinuclear complex[3] $[CoCp(\mu\text{-}CO)]_2$, **2**, as an intermediate.[4]

The carbonyl stretch for **1** is observed at 1725 cm^{-1} in KBr and 1710 cm^{-1} in toluene. This value is approximately 70 cm^{-1} lower than the stretch observed for **2** and is consistent with a change in the coordination geometry of the carbonyls from doubly to triply bridging.[5] The mass spectrum (EI) of **1** shows a small peak at *m/e* = 428 corresponding to the parent ion as well as prominent peaks for **2** and $(CoCp)_4(CO)_2$,[6] **3**. The thermal decomposition

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[4] Addition of $CpCo(C_2H_4)_2$ to the preformed dinuclear intermediate produces the tricobalt cluster. A satisfactory elemental analysis for **1** has been obtained.

[5] These values are close to those reported for complexes similar to **1** which contain triply bridging carbonyls: $Cp_3Ni_3(CO)_2$,[1a] 1742; $CpCoCp_2Ni_2(CO)_2$,[1a] 1737; $Cp^*{}_3Co_3(CO)_2$,[1b] 1680 cm^{-1}.

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Table I. Structural Comparisons between Isostructural $Cp_3M_3(CO)_2$ Analogues

complex[a]	electrons	M–M	M–CO	C–O	M–$Cp_{centroid}$
$Cp_3Co_3(CO)_2$[b]	46	2.390 (1)	1.973 (4)	1.180 (6)	1.70
$Cp^*{}_3Co_3(CO)_2$[c]	46	2.370 (1)	1.951 (6)	1.190 (10)	1.73
$CpCoCp_2Ni_2(CO)_2$[d]	48	⟨2.358⟩[e]	⟨1.933⟩[e]	1.183 (13)	⟨1.73⟩[e]
$Cp_3Ni_3(CO)_2$[d]	49	2.389 (2)	1.932 (9)	1.183 (13)	1.76

[a] All complexes crystallize in the space group $P6_3/m$ and exhibit the same crystallographic site symmetry. [b] This work. [c] Reference 1b. [d] Reference 1a. [e] Average values due to 3-fold disorder of the trinuclear core.

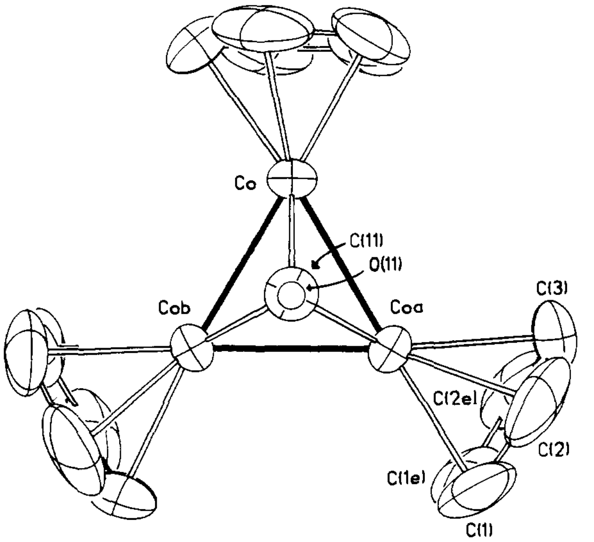

Figure 2. Molecular structure of $Cp_3Co_3(CO)_2$, (**1**). Bond distances are given in Table I. Important bond angles (deg) are as follows: C(11)–Co–Co(A) = 52.7(1), C(11)–Co–C(11a) = 91.2(2), O(11)–C(11)–Co = 135.6(2).

of **1** under the high vacuum conditions of the mass spectrum experiment is mimicked in solution where smooth decomposition to **2** and **3** is observed (vide infra).

The ^1H NMR spectrum of **1** exhibits a sharp singlet ($\Delta\nu$ = 20 Hz) at −33 ppm (upfield of TMS) in benzene-d_6 (22 °C). The temperature dependence of this signal is shown in Figure 1. The linear behavior of the chemical shift of this signal with inverse temperature satisfies the Curie law and suggests that the complex exists in a single spin state in this temperature range.[7] Solution magnetic susceptibility measurements (Evans method) give an effective magnetic moment of 3.0 ± 0.2 μ_B for **1**. This value, in addition to the even valence electron count for **1** requires that its paramagnetism be derived from a triplet state. Preliminary solid-state magnetic susceptibility measurements, however, indicate that **1** becomes diamagnetic at temperatures below 100 K, and the ground state may actually be a singlet.

Single crystals of **1** were obtained[8] and subjected to X-ray structural analysis. C_{3h} site symmetry (D_{3h} for the $M_3(CO)_2$ core) is imposed on the molecule for the hexagonal space group $P6_3/m$.[9] This requires that the two capping carbonyls lie on the 3-fold rotation axis, while the three cobalt atoms form an equilateral triangle and reside in the horizontal mirror plane. A view of the complex down the 3-fold axis is shown in Figure 2. Structural data of interest for **1** and several other isomorphous trinuclear clusters are summarized in Table I.

As can be seen in Table I, the structures of the four complexes are similar with all corresponding M–M and M–carbonyl distances within 0.04 Å of one another. In particular, the Co–Co distance in **1** and the Ni–Ni distance in $Cp_3Ni_3(CO)_2$ are identical within experimental error. According to several molecular orbital calculations[10] concerning $Cp_3M_3(CO)_2$ clusters, the ordering and character of the MO's in these clusters remain similar for the different combinations of metals. The singly occupied HOMO (a_2') of the trinickel analogue is M–M antibonding and should cause the trimetal core to expand relative to lower electron counts. Comparison of the M–M distances between the 48e^- $CpCoCp_2Ni_2(CO)_2$ and trinickel complex are in agreement with this prediction. However, the equality of the Co–Co and Ni–Ni distances in **1** and the Ni_3 complex does not support this prediction.[11] One reason for the unexpectedly long Co–Co distance may involve the high-spin nature of the tricobalt cluster.[12] Additionally, the covalent radius of the Ni^+ ion is slightly smaller than that of Co^+.

When $Cp_3Co_3(CO)_2$ is dissolved in degassed benzene, toluene, or THF, smooth decomposition to dinuclear **2** and tetranuclear **3** is observed. In benzene, the reaction follows clean, first-order equilibrium kinetics for greater than 90% reaction (K_{eq} = 4, k_{rate} = 3.0 (7) × 10^{-5} s^{-1}, T = 40 °C). To check that the equilibrium is truly reversible, a benzene-d_6 solution of **2** and **3** was allowed to stand in the dark for 2 days. An NMR spectrum of the resulting product mixture clearly showed the presence of **1** in addition to the starting materials. A mechanism consistent with the above entails a dissociative slow step whereby the dinuclear product **2** and a solvated "CpCo" fragment is formed. This mononuclear species is then captured by a second molecule of **1** to give the other final product, **3**. Support for this sequence of steps is found in preliminary trapping studies where added trapping reagents completely suppress the formation of the tetranuclear product **3**, while not affecting the formation of **2**. This reaction is considerably accelerated in THF.[13]

The cluster $(CpCo)_3(CO)_2$ represents one extreme in this series of trinuclear clusters and is of interest both for its predicted high spin ground state as well as high reactivity. It is electron deficient due to its 46e^- valence count and due to the relatively poor donating ability of the Cp ligands. The high spin ground state (S = 1) indicated by its magnetic behavior is consistent with previous theoretical studies and the high molecular symmetry observed in the solid state. It is of interest to note in this regard that *every* other 46e^-, mixed-metal cluster currently known which contains at least one CpCo fragment also exhibits some form of high spin triplet or single ⇄ triplet spin equilibrium.[2a] Finally, this new complex appears to be separated from other polynuclear cobalt

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[7] The analogous Cp* complex, $Cp^*{}_3Co_3(CO)_2$ exhibits more complex shift vs $1/T$ behavior indicative of a single ⇄ triplet spin equilibrium.[1b]

[8] The reaction of $CpCo(C_2H_4)_2$ with $Cp_2Ti(CO)_2$ produces the known cluster, $[Cp_2Ti]_2[(CpCo)_3(CO)_2]$: Gambarotta, S.; Stella, S.; Floriani, C.; Chiesti-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 254–255. In the course of studying this reaction, our attempts to recrystallize the product from hexane/THF mixtures gave instead single crystals of **1**. The same behavior is observed for the analogous zirconium complex. Crystals of **1** prepared in this manner have identical spectral properties as samples prepared according to the description in the text.

[9] R_f = 3.29%, R_{wf} = 3.84%, GOF = 1.054, data/parameter = 20.7, largest residual peak = 0.596 e/$Å^{-3}$ (within Cp ring). Further details of the structure refinement are given in the Supplementary Material.

[10] Several molecular orbital studies on **1** and similar systems have appeared. $Cp_3Co_3(CO)_2$: Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456–3467. (See also footnote 50 of ref 1b.) $Cp_3Ni_3(CO)_2$: Rives, A. B.; Xiao-Zeng, Y.; Fenske, R. F. *Inorg. Chem.* **1982**, *21*, 2286–2294. $Cp_3Rh_3(CO)_2$: Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta.* **1980**, *63*, 29–49.

[11] The structure of $Cp^*{}_3Co_3(CO)_2$ indicates steric interactions between Cp rings do not play a significant role in determining the size and shape of the trimetal core.

[12] High and low spin Fe(III) porphyrin complexes exhibit dramatic elongation of M–N distances with spin state changes: (a) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992–1996. (b) Hoffman, A. B.; Collins, D. M.; Day, V. W.; Fleischer, E. B.; Srivastava, T. S.; Hoard, J. L. *Ibid.* **1972**, *94*, 3620–3626. (c) Collins, D. M.; Countryman, R.; Hoard, J. L. *Ibid.* **1972**, *94*, 2066–2072.

[13] Some type of solvent assistance is indicated in THF. The rate law is again first-order, K_{obs} = 9 (1) × 10^{-4} s^{-1} (−50 °C). Further studies are in progress.

clusters by low kinetic barriers. Further studies of the properties and reactivity of this complex are in progress.

Acknowledgment. This research was supported by a PRF-AC (21056-AC3) grant. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Johnson Matthey Company for their generous loan of precious metal starting materials for this research.

Supplementary Material Available: Details of the structure refinement and tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates (3 pages); table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Chiral Recognition of Aromatic Carboxylate Anions by an Optically Active Abiotic Receptor Containing a Rigid Guanidinium Binding Subunit

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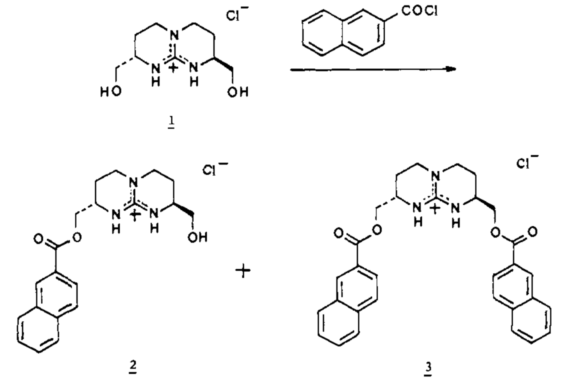
Molecular recognition by abiotic synthetic receptors is an important goal in current bioorganic chemistry. To achieve selectivity, a number of recognition features (i.e., electrostatic or hydrophobic interactions, hydrogen bonds) must be incorporated to the molecular receptor to complement, in a multiple point binding, the chemical characteristics of the substrate.[2] For anionic substrates, positively charged or electron-deficient binding sites are required.[3] This may be accomplished either by Lewis acid-containing receptors,[4] by ammonium quaternary salts,[5] or by protonated polyamines[6] and guanidines.[7] The guanidinium group (pK_a ca. 13.5) remains protonated over a much wider range of pH than does the ammonium group and forms characteristic pairs of well-organized, strong zwitterionic hydrogen bonds ($N-H^+\cdots O^-$) with carboxylates or phosphates. Nature offers a number of examples of this bonding pattern, involving the arginine side chains of proteins.[8]

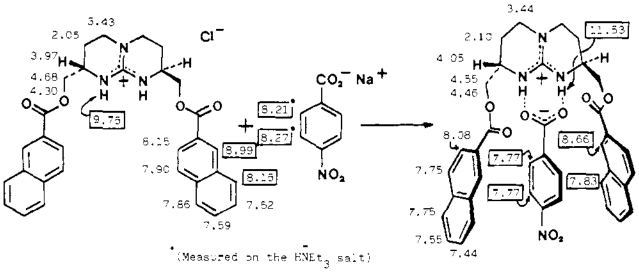
We recently described the synthesis of the rigid bicyclic guanidine subunit **1**, which was assembled in nine steps from asparagine. Both enantiomers **1**-*SS* and **1**-*RR* were obtained in excellent optical purity from L- and D-asparagine, respectively.[9] We present herein evidence for the complexation of aromatic carboxylic oxoanions by a bis-naphthoyl derivative of **1** and the first example of chiral recognition of anions, namely the enantiomers of the sodium salt of *N*-acetyltryptophan.

Reaction of **1** with 2-naphthoyl chloride (3 equiv) in dry *N*,*N*-dimethylformamide with an excess of triethylamine afforded a mixture of the mono- and bis-naphthoyl esters, **2** and **3**, in 20% and 58% yields, respectively (eq 1).[10]



(1)

Sodium *p*-nitrobenzoate was quantitatively extracted from water by a chloroform solution of **3**. Despite its ionic structure, no traces of **3** were found in the water layer, and the chloroform extract was composed exclusively by the *p*-nitrobenzoate guanidinium salt (eq 2). The ^{1}H NMR spectrum revealed significant shifts for most signals of both ions in the 1:1 complex. For instance, NH guanidinium protons showed a 1.78 ppm downfield shift relative to **3**, whereas most aromatic protons of the host and the guest shifted upfield. Moreover, both multiplets corresponding to the methylene protons of the host side arms approached each other from 0.40 to 0.09 ppm apart. These data strongly support formation of a complex of a well-defined geometry, involving a double recognition of the guest by the guanidinium cation (zwitterionic hydrogen bonds with the carboxylate function) and the naphthoyl



(2)

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[1] (a) Instituto de Química Orgánica, CSIC. (b) Universidad Autónoma de Madrid. (c) Université Louis Pasteur.

[2] (2) Relevant examples have been provided recently to illustrate this concept: (a) Rebek, J.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476. (b) Rebek, J.; Askew, B.; Nemeth, D.; Parris, K. *Ibid.* **1987**, *109*, 2432. (c) Rebek, J.; Askew, B.; Ballester, P.; Doa, M. *Ibid.* **1987**, *109*, 4119. (d) Jeong, K. S.; Rebek, J. *Ibid.* **1988**, *110*, 3327 and references therein. (e) Hamilton, A. D.; Van Engen, D. *Ibid.* **1987**, *109*, 5035. (f) Pant, N.; Hamilton, A. D. *Ibid.* **1988**, *110*, 2002.

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[5] For quaternary ammonium containing macropolycycles, see Schmidtchen, F. P. (a) *Angew. Chem., Int. Ed. Engl.* **1977**, *20*, 720. (b) *Chem. Ber.* **1980**, *113*, 864. (c) *Ibid.* **1981**, *114*, 597. (d) *Ibid.* **1984**, *117*, 725 and 1287. (e) *J. Chem. Soc., Perkin Trans. 2* **1986**, 135.

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[9] Echavarren, A.; Galán, A.; de Mendoza, J.; Salmerón, A.; Lehn, J.-M. *Helv. Chim. Acta* **1988**, *71*, 685.

[10] Both compounds were separated by flash silica gel chromatography (15:1 dichloromethane-methanol) and fully characterized by combustion analysis and ^{1}H and ^{13}C NMR spectroscopy. Data for **3**: mp 206-207 °C; $[\alpha]^{20}_D = +123.0°$ and $-117.4°$ for the (*SS*) and (*RR*) enantiomers, respectively (c = 0.5, $CHCl_3$).

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