Inorg. Chem. **1980**, *19*, 1221–1226

separation for the progressions was 344 ± 10 cm^{-1} for the tetraglycine complex and 347 ± 5 cm^{-1} for the leucine complex. Again only this one value is observed for all progressions.

It is interesting that for both of the tetrakis(amino acid) complexes studied the oriented gas polarization ratios are strictly satisfied while for the tetracarboxylic acid compounds they are not. The only obvious difference between these two classes of compound is that the amino acid complexes are 4+ ions with charges on the periphery because of the zwitterionic nature of the amino acids, while the tetracarboxylates crystallize as a van der Waals packing of neutral molecules. The ionic nature of the former type of crystal could lead to the observed accurate alignment of the transition moments for two reasons. First, the presence of intervening anions causes the intermolecular distances to be larger, and this should result in less intermolecular borrowing of intensity. It is this borrowing that causes a shift of the transition moment from that of the molecular axes. Second, the highly anisotropic field created by the charge distribution in the ionic crystal may force the transition moment to align with the molecular axes.

Conclusions. The spectral results of the present study are in remarkably close agreement with those obtained for $[Mo_2(O_2CCH_2NH_3)_4](SO_4)_2 \cdot 4H_2O$, except that the low-energy, weak progression in *z* polarization is absent. We feel that this affords a strong indication that this progression is spurious and probably, as suggested by Martin, Newman, and Fanwick,[6] originates in an impurity. The three progressions that are genuinely due to the $[Mo_2(O_2CCRNH_3)_4]^{4+}$ ions in each case can then be fully reconciled with the $\delta^* \leftarrow \delta$ assignment, exactly as shown by Martin, Newman, and Fanwick in the case of $Mo_2(O_2CCH_3)_4$.

Acknowledgment. We are grateful to the National Science Foundation for support of this research, including funds for the building of the spectrometer.

Registry No. Mo_2(L-leucine)$_4Cl_2$(pts)$_2 \cdot 2H_2O$, 72845-27-3; $K_4Mo_2Cl_8$, 25448-39-9.

Supplementary Material Available: A table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of π-Toluene Complexes of $(C_6F_5)_2Co$ and $(C_6F_5)_2Ni$

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$(\pi\text{-}C_6H_5CH_3)Co(C_6F_5)_2$ and $(\pi\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$ crystallize in space group *Pnma* with four molecules per unit cell. The structures were determined from 1335 and 1741 observed diffractometer data and refined to *R* values of 6.1 and 5.2% for the cobalt and nickel compounds, respectively. The structures consist of the metal atoms σ bonded to two C_6F_5 groups and π bonded to one toluene ligand in an arrangement of *m*(*Cs*) symmetry which is fully utilized crystallographically. Relatively short M–C σ bonds of 1.931 (5) Å for the cobalt compound and 1.891 (4) Å for the nickel compound are observed while the M–ring distances are 1.627 Å (Co) and 1.681 Å (Ni). The longer π bonds in the nickel compound suggest that the additional electron (Co → Ni) resides in an orbital that is antibonding with respect to the arene ligand. The toluene ligand is planar in the cobalt complex but a small "boat" type distortion amounting to a rotation of the two end carbons of ~4° away from the metal is observed in the nickel complex.

Introduction

Examples of π-arene complexes of the group 8 metals include M(0),[1] M(I),[2] M(II),[3] and M(III)[4] species.[5] In recent years these complexes have attracted a good deal of interest for a variety of reasons including their catalytic properties[6] and, in particular, the observation that the π-arene ligand can be extremely labile in solution.[7,8] This lability is of fundamental importance since the dissociation of a π-arene ligand generates three possible coordination sites.

Because of the new synthetic procedures available to us and the limited extent of structural data available in general on π-arene complexes, we have established a vigorous program to characterize structurally a series of cobalt(II) and nickel(II) complexes. Previously, we have reported the synthesis of the first example of an R_2M–π-arene complex,[9] $(C_6F_5)_2Co$–π-toluene, and the preliminary results of an X-ray structure determination. More recently, we have reported the synthesis and some of the interesting chemistry of the analogous nickel(II) compound.[8] Herein, we report the complete results of the structure determination of the paramagnetic $(C_6F_5)_2Co$–π-toluene complex and also the results of a structure deter-

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mination of the diamagnetic $(C_6F_5)_2Ni$–π-toluene complex. This study represents the first example of a direct comparison between isostructural π-arene group 8 metal complexes.

Experimental Section

Dark amber crystals of the compounds were produced under a nitrogen atmosphere by slowly stripping solvent (toluene) followed by refrigeration of the sample. Crystals used for data collection had the following dimensions: cobalt compound 0.25 × 0.28 × 0.30 mm; nickel compound 0.62 × 0.42 × 0.22 mm.

Precession photographs led to the assignment of space group *Pnma* (No. 62).[10] Lattice constants determined on the diffractometer at ambient room temperature were as follows: cobalt compound a = 11.465 (9), b = 16.025 (12), c = 9.503 (8) Å; nickel compound a = 11.493 (4), b = 15.865 (6), c = 9.533 (3) Å. The calculated densities for four molecules of $C_6H_5CH_3(C_6F_5)_2M$ per unit cell volume were 1.845 and 1.854 g/cm^3 for the cobalt and nickel compounds, respectively.

Intensity data were collected on a Picker card-controlled diffractometer using Mo Kα radiation and a takeoff angle of ~3°. Each peak was scanned in 2θ at the rate of 1°/min and background counts were of 20-s duration. Three standards were monitored after every 100 data to check for crystal and instrument stability. For the cobalt compound, data were collected to a limiting 2θ of 52.87° (0.9 Cu spheres). Within this range five reflections were inadvertently not measured. The larger crystal of the nickel compound provided data to a limiting 2θ of 58.66° (1.2 Cu spheres). The intensity of the standards remained statistically constant for the cobalt compound but decreased linearly by 11% over the course of data collection on the nickel compound. The crystal was recentered once about midway through the data set because of crystal movement, but the linear decay of the standards continued. Minor scaling corrections were applied to the data from the linear equation obtained by the least-squares fit of intensity vs. exposure time.

Intensity data were reduced to a set of $|F_o|$'s by application of Lorentz and polarization corrections (Lp). Standard deviations were calculated according to

$$\sigma_F = [(C + k^2B)/4|F_o|^2(Lp)^2]^{1/2}$$

where C and B are the counts of the scan and sum of the backgrounds, respectively, and k is the ratio of scan time to total background counting time. Reflections were taken as observed if $|F_o| > 3\sigma_F$. This amounts to 1335 data for the cobalt compound and 1741 for the nickel compound.

Patterson and Fourier[11] techniques were used to locate all atoms in the cobalt compound. Because the nickel compound was isostructural, these coordinates (except hydrogens) were used as initial parameters for the nickel compound.[6] The parameters were refined by using unit-weighted full-matrix least squares[12] followed by fully anisotropic refinement. Atomic coordinates of the ring hydrogen atoms were located from difference syntheses and included in further refinement with fixed thermal parameters. Anomalous dispersion corrections were used for the metal atoms.[13] R values at this stage were 6.4 and 5.8% for the cobalt and nickel compounds, respectively, where $R = \sum||F_o| - |F_c||/\sum|F_o|$. Empirical weights ($w = 1/\sigma^2$) were then calculated from

$$\sigma = \sum_0^3 a_n|F_o|^n$$

where a_n are the coefficients from the least-squares fit of

$$||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$$

Absorption corrections were then applied to the data on the nickel compound. Transmission factors ranged from 0.871 to 0.776. Final refinements of the 150 structural parameters using this weighting scheme produced R = 6.1% and R_w = 5.8% for the cobalt compound and R = 5.2% and R_w = 6.6% for the nickel compound, where $R_w = [\sum w(|F_o|)^2/\sum w|F_o|^2]^{1/2}$. The error of fit was 1.39 and 1.43 for the cobalt and nickel compounds, respectively. Changing to the $1/\sigma^2$ weighting decreased the Co–C_1 distance by 0.009 Å while the other average bond parameters were not changed significantly. In the nickel compound the $1/\sigma^2$ weighting decreased the average Ni–C π-bond distance by 0.008 Å, and the average C–C bond distance within the toluene ligand decreased by 0.01 Å. Final difference syntheses revealed the largest residual electron density for the cobalt compound was 0.67 e/Å^3 while residuals for the nickel compound ranged from 0.49 to −0.51 e/Å^3.

Table I. Atomic Coordinates in $(\eta^6\text{-}C_6H_5CH_3)Co(C_6F_5)_2$ [a]

atom	10^4x	10^4y	10^4z
Co	1949 (1)	2500	−74 (1)
C_1	969 (4)	1660 (3)	778 (5)
C_2	1183 (5)	1340 (3)	2090 (6)
C_3	493 (6)	745 (4)	2732 (6)
C_4	−475 (6)	460 (4)	2051 (7)
C_5	−729 (5)	750 (4)	729 (7)
C_6	−5 (4)	1343 (3)	138 (6)
C_7	2498 (7)	2500	−2271 (8)
C_8	2821 (5)	1760 (4)	−1605 (7)
C_9	3472 (5)	1764 (5)	−354 (7)
C_{10}	3815 (7)	2500	260 (11)
C_{11}	1784 (10)	2500	−3611 (9)
F_2	2133 (3)	1598 (2)	2824 (3)
F_3	752 (4)	450 (3)	4022 (4)
F_4	−1174 (4)	−106 (2)	2668 (5)
F_5	−1663 (3)	462 (2)	39 (5)
F_6	−2829 (3)	1601 (2)	−1181 (4)
H_8	2584 (63)	1323 (40)	−1919 (74)
H_9	3641 (59)	1208 (38)	99 (66)
H_{10}	4149 (86)	2500	1093 (100)

[a] Estimated standard deviations are given in parentheses for the least significant digit.

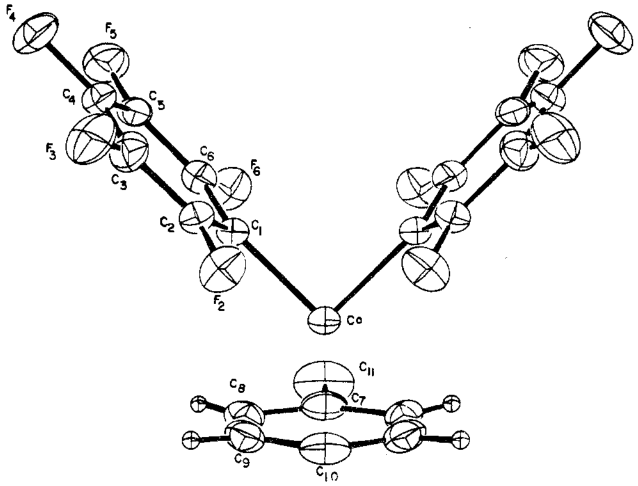

Figure 1. A traced ORTEP drawing of one molecule of $(\pi\text{-}C_6H_5CH_3)Co(C_6F_5)_2$ displaying the thermal ellipsoids at 25% probability and showing the numbering scheme of the asymmetric unit of structure. Hydrogen atoms are numbered according to the carbon to which they are attached. The hydrogen atoms have been reduced in size and H_{10} has been eliminated for clarity.

Atomic coordinates from the final refinement and the associated anisotropic thermal parameters are listed in Tables I–IV for the cobalt and nickel compounds, respectively.

Results and Discussion

A traced computer drawing of the cobalt complex as it exists in the crystal is shown in Figure 1. The thermal ellipsoids listed in Table II are displayed at 25% probability, and the atomic numbering scheme is given for the asymmetric unit of structure. The size of the hydrogen atoms has been de-

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Table II. Anisotropic Thermal Parameters[a] in $(\eta^6\text{-}C_6H_5CH_3)Co(C_6F_5)_2$

atom[b]	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	3.18 (4)	3.90 (4)	3.41 (4)		0.46 (4)	
C_1	3.0 (2)	3.6 (2)	4.0 (2)	0.0 (2)	0.6 (2)	−0.1 (2)
C_2	4.2 (2)	4.2 (2)	4.2 (2)	−0.1 (2)	0.7 (2)	0.1 (2)
C_3	6.4 (3)	4.8 (3)	4.6 (3)	−0.3 (3)	1.4 (3)	0.4 (2)
C_4	5.3 (3)	4.2 (3)	6.7 (4)	−0.8 (2)	2.3 (3)	−0.1 (3)
C_5	3.5 (2)	4.8 (3)	6.9 (3)	−0.2 (2)	0.8 (2)	−1.8 (3)
C_6	3.9 (2)	4.0 (2)	4.7 (3)	0.2 (2)	0.5 (2)	−0.3 (2)
C_7	3.9 (3)	7.1 (5)	3.8 (4)		1.3 (3)	
C_8	4.4 (2)	5.4 (3)	5.3 (4)	−0.1 (3)	1.6 (3)	−1.4 (3)
C_9	4.0 (3)	6.1 (3)	6.9 (4)	1.5 (2)	1.3 (2)	0.9 (3)
C_{10}	3.2 (3)	8.7 (7)	6.1 (5)		0.1 (4)	
C_{11}	7.5 (6)	13.7 (9)	3.8 (4)		−0.9 (4)	
F_2	6.4 (2)	7.2 (2)	4.7 (2)	−1.4 (2)	−1.3 (1)	1.5 (1)
F_3	10.3 (3)	8.0 (2)	5.9 (2)	−1.7 (2)	1.2 (2)	2.9 (2)
F_4	8.5 (2)	6.7 (2)	10.1 (3)	−3.1 (2)	3.8 (2)	0.5 (2)
F_5	4.5 (2)	7.4 (2)	10.5 (2)	−1.7 (1)	0.1 (2)	−2.5 (2)
F_6	5.5 (2)	7.1 (2)	6.2 (2)	−0.6 (2)	−1.9 (2)	0.3 (2)

[a] Estimated standard deviations are given in parentheses for the least significant digits. $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$, where β_{ij} are the unitless parameters used in refinement in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Isotropic thermal parameters of the hydrogen atoms are fixed at 7 Å^2.

Table III. Atomic Coordinates in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$

atom	10^4x	10^4y	10^4z
Ni	1944.6 (6)	2500	−24.3 (8)
C_1	972 (3)	1675 (3)	796 (4)
C_2	1194 (4)	1350 (3)	2107 (5)
C_3	502 (5)	749 (3)	2730 (5)
C_4	−461 (5)	463 (3)	2062 (7)
C_5	−714 (4)	759 (3)	741 (7)
C_6	2 (4)	1355 (3)	134 (6)
C_7	2518 (6)	2500	−2282 (7)
C_8	2828 (4)	1755 (3)	−1611 (6)
C_9	3503 (5)	1765 (4)	−379 (6)
C_{10}	3878 (6)	2500	205 (9)
C_{11}	1830 (8)	2500	−3630 (8)
F_2	2141 (3)	1606 (2)	2833 (3)
F_3	767 (4)	446 (2)	4014 (4)
F_4	−1158 (3)	−110 (2)	2672 (4)
F_5	−1649 (3)	465 (2)	46 (4)
F_6	−267 (3)	1609 (2)	−1173 (3)
H_8	2540 (60)	1230 (40)	−1850 (60)
H_9	3680 (60)	1310 (40)	70 (60)
H_{10}	4290 (80)	2500	1140 (90)

liberately reduced for clarity. The structures consist of discrete molecules with the metal atom σ bonded to two perfluorophenyl groups and π bonded to toluene in an arrangement of $m(Cs)$ symmetry. The crystallographic mirror plane contains the metal atom, C_7, C_{10}, C_{11}, and H_{10}.

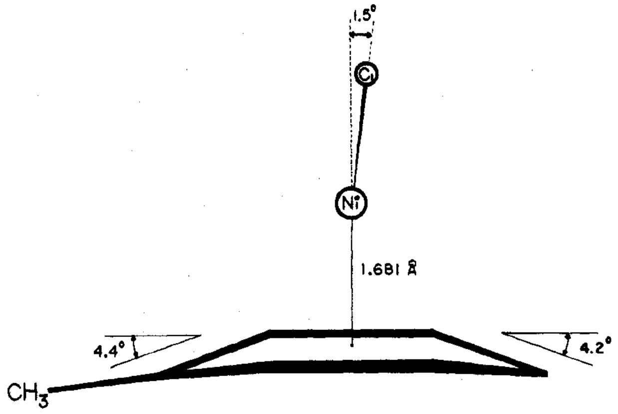

Figure 2. The orientation of the Ni and the two σ-bonded carbons with respect to the toluene ligand in $(\pi\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$.

The carbon atoms in the perfluorophenyl rings are planar with the largest deviation being 0.01 Å and the average deviation being 0.004 Å (Co) and 0.006 Å (Ni). The F atoms deviate an average of 0.02 Å (Co) and 0.03 Å (Ni) from the mean plane of the carbons. The average C–C bond distances of 1.373 (9) Å (Co) and 1.374 (7) Å (Ni) are in agreement with other reported values for the C_6F_5 group in metal complexes.[14,15] Similarly, the average C–F distances of 1.349 (7)

Table IV. Anisotropic Thermal Parameters[a] in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	2.82 (3)	3.55 (3)	3.20 (3)	0.00	0.27 (3)	0.00
C_1	3.1 (2)	3.5 (2)	3.7 (2)	0.1 (1)	0.5 (1)	−0.4 (1)
C_2	4.5 (2)	3.8 (2)	3.8 (2)	−0.1 (2)	0.8 (2)	−0.1 (2)
C_3	6.4 (3)	4.4 (2)	4.4 (2)	−0.3 (2)	2.0 (2)	0.6 (2)
C_4	5.2 (3)	4.2 (2)	7.1 (3)	−1.1 (2)	2.7 (2)	−0.1 (2)
C_5	3.1 (2)	4.2 (2)	8.1 (3)	−0.5 (2)	1.2 (2)	−1.9 (2)
C_6	3.6 (2)	4.0 (2)	5.3 (2)	0.1 (1)	0.2 (2)	−0.4 (2)
C_7	3.7 (3)	6.6 (4)	3.1 (3)	0.00	0.8 (2)	0.00
C_8	4.2 (2)	4.8 (2)	5.4 (2)	−0.1 (2)	1.5 (2)	−1.0 (2)
C_9	4.0 (2)	5.9 (3)	6.1 (3)	1.6 (2)	1.0 (2)	1.0 (2)
C_{10}	2.8 (2)	8.0 (5)	5.6 (4)	0.00	0.1 (3)	0.00
C_{11}	6.5 (5)	14.4 (8)	3.0 (3)	0.00	−0.9 (3)	0.00
F_2	6.4 (2)	6.3 (2)	4.5 (1)	−1.3 (1)	−1.6 (1)	1.3 (1)
F_3	10.6 (2)	7.3 (2)	5.8 (2)	−1.2 (2)	1.7 (2)	2.6 (2)
F_4	8.5 (2)	6.2 (2)	10.6 (3)	−3.1 (2)	4.4 (2)	−0.1 (2)
F_5	4.5 (1)	6.7 (2)	10.9 (3)	−1.6 (1)	0.1 (2)	−2.8 (2)
F_6	5.5 (1)	6.6 (2)	5.9 (2)	−0.7 (1)	−2.3 (1)	0.3 (1)

[a] Estimated standard deviations are given in parentheses for the least significant digits. $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$, where β_{ij} are the unitless parameters used in refinement in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Isotropic thermal parameters of the hydrogen atoms are fixed at 7 Å^2.

Table V. Bond Distances (Å) in $(\eta^6\text{-}C_6H_5CH_3)Co(C_6F_5)_2$

	Within the Ligands		
C_1-C_2	1.370 (7)	C_5-F_5	1.337 (6)
C_2-C_3	1.381 (7)	C_6-F_6	1.358 (7)
C_3-C_4	1.365 (8)	C_7-C_8	1.395 (8)
C_4-C_5	1.371 (9)	C_8-C_9	1.404 (9)
C_5-C_6	1.381 (8)	C_9-C_{10}	1.374 (8)
C_6-C_1	1.370 (7)	C_7-C_{11}	1.51 (1)
C_2-F_2	1.358 (6)	C_8-H_8	0.81 (6)
C_3-F_3	1.347 (7)	C_9-H_9	1.01 (6)
C_4-F_4	1.345 (7)	C_{10}-H_{10}	0.88 (9)
	Coordination Sphere		
Co-C_1	1.931 (5)	Co-C_9	2.124 (6)
Co-C_7	2.180 (8)	Co-C_{10}	2.163 (9)
Co-C_8	2.127 (6)		

Table VI. Bond Distances (Å) in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$

	Within the Ligands		
C_1-C_2	1.375 (6)	C_5-F_5	1.345 (6)
C_2-C_3	1.378 (6)	C_6-F_6	1.346 (6)
C_3-C_4	1.354 (7)	C_7-C_{11}	1.509 (10)
C_4-C_5	1.375 (8)	C_7-C_8	1.390 (6)
C_5-C_6	1.381 (7)	C_8-C_9	1.408 (8)
C_6-C_1	1.378 (6)	C_9-C_{10}	1.362 (7)
C_2-F_2	1.352 (5)	C_8-H_8	0.92 (6)
C_3-F_3	1.350 (6)	C_9-H_9	0.86 (6)
C_4-F_4	1.344 (5)	C_{10}-H_{10}	1.01 (9)
	Coordination Sphere		
Ni-C_1	1.891 (4)	Ni-C_9	2.164 (5)
Ni-C_7	2.251 (6)	Ni-C_{10}	2.232 (7)
Ni-C_8	2.171 (5)		

Table VII. Bond Angles (Deg) in $(\eta^6\text{-}C_6H_5CH_3)Co(C_6F_5)_2$

$C_6C_1C_2$	114.3 (5)	$C_1C_6F_6$	119.2 (5)
$C_1C_2C_3$	123.9 (5)	$C_8C_7C_8'$	116.6 (8)
$C_2C_3C_4$	119.2 (6)	$C_{11}C_7C_8$	121.7 (4)
$C_3C_4C_5$	119.6 (5)	$C_7C_8C_9$	121.4 (6)
$C_4C_5C_6$	118.6 (6)	$C_7C_8H_8$	119 (5)
$C_5C_6C_1$	124.4 (6)	$C_9C_8H_8$	120 (5)
$C_1C_2F_2$	119.8 (5)	$C_8C_9C_{10}$	121.1 (7)
$C_3C_2F_2$	116.3 (5)	$C_8C_9H_9$	117 (4)
$C_2C_3F_3$	121.3 (6)	$C_{10}C_9H_9$	121 (4)
$C_4C_3F_3$	119.5 (6)	$C_9C_{10}C_9'$	118.4 (9)
$C_3C_4F_4$	120.3 (6)	$C_9C_{10}H_{10}$	120.5 (7)
$C_5C_4F_4$	120.1 (6)	C_1CoC_1'	88.3 (3)
$C_4C_5F_5$	120.2 (6)	C_7CoC_8	37.8 (2)
$C_6C_5F_5$	121.3 (6)	C_8CoC_9	38.6 (3)
$C_5C_6F_6$	116.4 (5)	C_9CoC_{10}	37.4 (2)

Å (Co) and 1.347 (6) Å (Ni) are also in greement with other metal complexes of C_6F_5 (Tables V and VI).[14,15]

Bond angles within the C_6F_5 ligands (Tables VII and VIII) show the expected trends.[16] In particular, the internal angles at the C_1 carbons are ~5° less than 120°. An angle less than 120° is expected because of the electropositive nature of the metal considering σ bonding alone and any π bonding should serve to further decrease this angle.[16]

Within the π-toluene ligands C–C bond distances average 1.391 (9) Å in the cobalt complex and 1.387 (8) Å in the nickel complex while the C_7–C_{11} distance is 1.51 (1) Å in both compounds (Table IX). These bond distances are within experimental error to those reported for the π-toluene molecule in (π-toluene)tricarbonylchromium.[17]

Table VIII. Bond Angles (Deg) in $(\eta^6\text{-}C_6H_5CH_3)Ni(C_6F_5)_2$

$C_6C_1C_2$	115.4 (4)	$C_1C_6F_6$	120.0 (4)
$C_1C_2C_3$	122.9 (5)	$C_8C_7C_8'$	116.4 (6)
$C_2C_3C_4$	120.1 (5)	$C_{11}C_7C_8$	121.7 (3)
$C_3C_4C_5$	119.3 (5)	$C_7C_8C_9$	121.0 (5)
$C_4C_5C_6$	119.4 (5)	$C_7C_8H_8$	124 (4)
$C_5C_6C_1$	122.9 (5)	$C_9C_8H_8$	114 (4)
$C_1C_2F_2$	120.2 (4)	$C_8C_9C_{10}$	121.7 (6)
$C_3C_2F_2$	116.9 (4)	$C_8C_9H_9$	122 (4)
$C_2C_3F_3$	120.5 (5)	$C_{10}C_9H_9$	116 (4)
$C_4C_3F_3$	119.5 (5)	$C_9C_{10}C_9'$	117.8 (7)
$C_3C_4F_4$	120.6 (6)	$C_9C_{10}H_{10}$	120.6 (6)
$C_5C_4F_4$	120.0 (5)	C_1NiC_1'	87.7 (2)
$C_4C_5F_5$	120.2 (5)	C_7NiC_8	36.6 (2)
$C_6C_5F_5$	120.5 (6)	C_8NiC_9	37.9 (2)
$C_5C_6F_6$	117.1 (4)	C_9NiC_{10}	36.0 (2)

Table IX. Comparison of Some Selected Bond Parameters[a]

parameter	$(\pi\text{-}C_6H_5CH_3)$-$Co(C_6F_5)_2$	$(\pi\text{-}C_6H_5CH_3)$-$Ni(C_6F_5)_2$
M-C_σ, Å	1.931 (5)	1.891 (4)
av M-C_π, Å	2.141 (7)	2.192 (6)
⊥M–ring, Å	1.627	1.681
θ,[b] deg	0	4.2
ϕ,[c] deg	3.7	1.5

[a] Distances are in Å and angles in degrees. [b] θ is the angle of rotation of the two end carbons C_7 and C_{10} from the plane of C_8, C_9, C_8', C_9'. [c] ϕ is the angle between the MC_1C_1' plane and the line perpendicular to the toluene plane.

Table X. Mean Plane Calculations and Deviations of Individual Atoms[a,b]

$(C_6H_5CH_3)Co(C_6F_5)_2$		$(C_6H_5CH_3)Ni(C_6F_5)_2$	
atom	dev, Å	atom	dev, Å
	C_6F_5 Planes		
C_1*	0.001 (5)	C_1*	0.006 (4)
C_2*	0.002 (6)	C_2*	0.002 (5)
C_3*	−0.007 (6)	C_3*	−0.010 (5)
C_4*	0.009 (6)	C_4*	0.011 (5)
C_5*	−0.005 (6)	C_5*	−0.002 (5)
C_6*	0.002 (5)	C_6*	−0.006 (5)
Co	0.030 (3)	Ni	0.022 (1)
F_2	−0.013 (4)	F_2	−0.019 (3)
F_3	−0.014 (5)	F_3	−0.026 (4)
F_4	0.030 (4)	F_4	0.029 (4)
F_5	−0.017 (4)	F_5	−0.020 (4)
F_6	−0.036 (4)	F_6	−0.051 (3)
	$C_6H_5CH_3$ Planes		
C_7*	−0.015 (9)	C_7	−0.056 (7)
C_8*	0.008 (7)	C_8*	0.0
C_9*	0.007 (7)	C_9*	0.0
C_{10}*	−0.015 (10)	C_{10}	−0.051 (7)
C_8'*	0.008 (7)	C_8'*	0.0
C_9'*	0.007 (7)	C_9'*	0.0
Co	1.627 (2)	Ni	1.681 (1)
C_{11}	0.002 (11)	C_{11}	−0.105 (9)
H_8	0.08 (7)	H_8	0.15 (6)
H_9	0.07 (7)	H_9	0.05 (9)
H_{10}	0.08 (10)	H_{10}	0.05 (9)

[a] Equations were derived from the equally weighted refinement of those atoms indicated by an asterisk. [b] Prime notation indicates those atoms related by the mirror plane.

Figure 2 shows the orientation of the metal–carbon σ bonds with respect to the toluene ligand. The interplanar angle between the plane containing $C_1M\,C_1'$ and the toluene plane is 86.3° in the cobalt complex and 88.5° in the nickel complex. In both compounds the metal lies on the perpendicular line through the ring center. Thus, the deviation of the interplanar angle from 90° is due to a small tilting of the σ-bonded carbons toward the side of the ring opposite the methyl group as shown in Figure 2 for the nickel compound. The corresponding tilting

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(14) See: Sanz, F.; Daly, J. J. *J. Chem. Soc. A* **1972**, 1083 and references therein.

(15) Churchill, M. R.; Veidis, M. V. *Chem. Commun.* **1970**, 1099. Churchill, M. R.; Veidis, M. V. *J. Chem. Soc. A* **1971**, 3463. Churchill, M. R.; Veidis, M. V. *J. Chem. Soc., Dalton Trans.* **1972**, 670. Churchill, M. R.; Kalra, R. L.; Veidis, M. V. *Inorg. Chem.* **1973**, *12*, 1656.

(16) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *31*, 221.

(17) Van Meurs, F.; Van Koningsveld, H. *J. Organomet. Chem.* **1977**, *131*, 423.

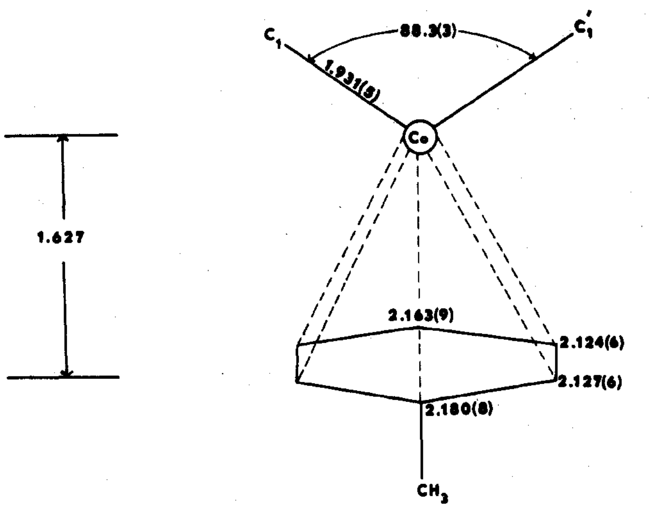

Figure 3. Bond parameters in the coordination sphere for (π-$C_6H_5CH_3$)$Co(C_6F_5)_2$.

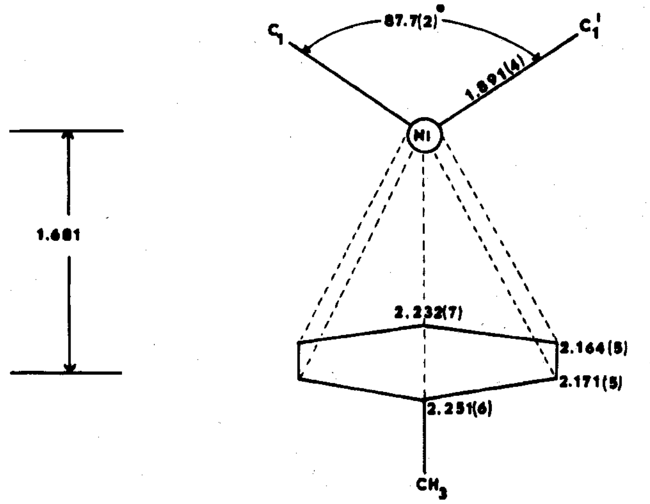

Figure 4. Bond parameters in the coordination sphere for (π-$C_6H_5CH_3$)$Ni(C_6F_5)_2$.

angle in the cobalt complex is 3.7°. An interesting difference in the two compounds is that the carbon framework of the π-toluene ligand is planar within experimental error in the cobalt complex (Table X); however, in the nickel complex the two end carbons, C_7 and C_{10}, are displaced by $\sim$0.05 Å away from the nickel atom. This displacement amounts to a rotation of the two end carbons of $\sim$4° from the four-carbon plane. Alternatively, this distortion could be described as a folding around the C_7–C_{10} vector of 5.2°. An effect of such a distortion would be a small tilting of the p orbitals on the four planar carbons toward the metal which would result in better overlap while the orbitals on C_7 and C_{10} would tilt away from the metal.

Bond parameters within the coordination spheres are given in Figures 3 and 4. The Co–C σ-bond length of 1.931 (5) Å is slightly shorter than the cobalt–mesitylene σ-bond length of 1.96 (1) Å[18] reported in *trans*-bis(diethylphenylphosphine)dimesitylcobalt(II). This would appear to be consistent with Churchill's[19] suggestion, by analogy with the systematic shortening observed for metal–carbon distances in perfluoroalkyls, that a similar shortening be associated with metal–perfluoroaryl distances when compared to metal–aryl distances. An analysis of our Ni–C σ bond does not support this generalization however. As Churchill points out, their results for (π-C_5H_5)$Ni(PPh_3)$ (σ_R) where R = C_6H_5 and C_6F_5 show no shortening, the Ni–C σ-bond distances being 1.904 (7) Å for C_6H_5 and 1.914 (14) Å for C_6F_5.[19] Our results for the Ni–C σ-bond length of 1.891(4) Å are within experimental error to their observed distance for C_6H_5. This anomaly notwithstanding, the observed M–C σ bonds in both structures are considerably shorter than estimates of "normal" M–C (sp^2) single bonds for Co(II) and Ni(II) and are only $\sim$0.1 Å longer than those in their respective carbonyls.[20] This could be interpreted as some multiple bonding to the metals which would help rationalize the remarkable stability of these compounds. Attempts to form similar complexes using other σ-bonding ligands have not yielded stable products thus far. The angle between these two σ-bonded carbons is $\sim$88° in both complexes.

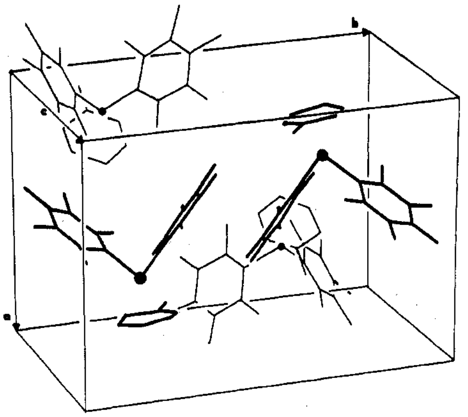

Figure 5. A unit cell diagram of (π-$C_6F_5CH_3$)$Ni(C_6F_5)_2$.

The average of the six Co–C π bonds is 2.141 Å and the average Ni–C π bond is 2.192 Å. The appearance of two different types of M–C π bonds is the result of small deviations of the carbon framework in the toluene ligand from regular hexagonal geometry. A small elongation is observed along the C_7–C_{10} axis together with a slight compression perpendicular to this axis.[21] Of course, the out of plane displacement in the nickel complex creates an even larger difference. The perpendicular cobalt to ring distance is 1.627 Å and the perpendicular nickel to four-carbon plane distance is 1.681 Å.

A packing diagram of the nickel compound is shown in Figure 5. The two shortest intermolecular interactions between fluorines and hydrogens occur between F_4–$H_8{}^{I}$ and F_3–$F_3{}^{II}$ where I is the symmetry operator $-x$, $-y$, $-z$ and II is the operator $-x$, $-y$, $1 - z$. In the cobalt complex the F_4–$H_8{}^{I}$ distance is 2.63 (6) Å and in the nickel complex the distance is 2.51 (6) Å. By use of the aromatic value for H, however, these distances are within a normal van der Waals contact of 2.47 Å.[22] The F_3–$F_3{}^{II}$ contacts are 2.917 (8) Å in the cobalt compound and 2.941 (7) Å in the nickel compound, which are close to the normal van der Waals contact of 2.94 Å.[22]

This work takes advantage of the rare opportunity of studying isostructural paramagnetic and diamagnetic complexes containing both M–arene σ and π bonds. Comparison of the bond parameters reveals that in going from Co(II) to

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(18) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 14.

(19) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 148.

(20) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91–164 and references therein.

(21) In the cobalt complex the elongation and compression relative to a regular benzene hexagon are both $\sim$0.05 Å, while in the nickel complex they are $\sim$0.05 and $\sim$0.07 Å, respectively. The corresponding values in (π-toluene)$Cr(CO)_3$[12] are both $\sim$0.03 Å. Some deviation of the carbon framework from hexagonal geometry is expected in free toluene because the bond angle at the CH_3 substituted carbon is expected to be <120° and the two bond distances to this carbon are expected to be slightly longer than in benzene.[16]

(22) Bondi, A. *J. Phys. Chem.* **1969**, *68*, 441.

Ni(II) the M–C σ bonds decrease by 0.04 Å while the perpendicular M–ring distance increases by ~0.05 Å. The shorter σ bond to Ni(II) is reasonable in terms of a nuclear charge effect. The longer π bonds, however, suggest that the highest occupied molecular orbital is antibonding or at least nonbonding with respect to the π-arene ligand.[23] It is hoped that additional structural and theoretical studies will lend insight into two important facets: (1) an understanding of the extreme π-arene lability in this series of compounds which are perhaps the most labile yet reported[5] and (2) an understanding of the significant structural differences that exist between the cobalt and nickel analogues with regard to M–arene π-bond lengths and with regard to distortions of the π-arene framework found in the Ni(II) case but not Co(II). Finally, a variety of other π-arene ligands are also under investigation.

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Registry No. (η^6-$C_6H_5CH_3$)Co(C_6F_5)$_2$, 60528-58-7; (η^6-$C_6H_5CH_3$)Ni(C_6F_5)$_2$, 66197-14-6.

Supplementary Material Available: Listing of the structure factor amplitudes is available (16 pages). Ordering information is given on any current masthead page.

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[23] A more detailed discussion of the bonding in this system of compounds including additional X-ray data and results of molecular orbital calculations will be forthcoming. Radonovich, L. J.; Albright, T. A.; Koch, F. J., work in preparation.

Contribution No. 6103 from the Division of Chemistry and Chemical Engineering,
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Crystal and Molecular Structure of a Mixed-Valent Copper(II)–Copper(I)–Macrocyclic Ligand Complex

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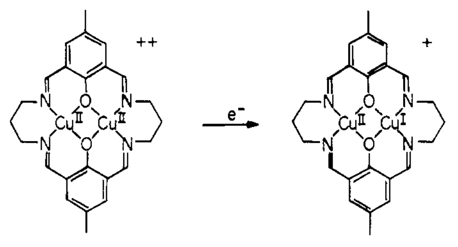
Condensation of 1,3-diaminopropane with 2-hydroxy-5-methylisophthalaldehyde in the presence of copper(II) perchlorate yields the binuclear copper(II)–macrocyclic ligand complex. One-electron electrochemical reduction gives the mixed-valent $Cu^{II}Cu^{I}$ ion **1**, which apparently exhibits facile electron transfer at 298 K. The crystal and molecular structure of **1** reveals distinct copper coordination sites in the solid state. Coordination about Cu1 is square planar with Cu–N bond lengths of 1.98 Å and Cu–O bond lengths of 1.96 Å. The second copper is disordered with 35% in the Cu2a site and 65% in the Cu2b site. The latter, Cu2b, is displaced 0.15 Å from the best plane of two oxygen (Cu2b–O = 2.12 Å) and two nitrogen (Cu2b–N = 1.96 Å) ligands toward an aromatic ring carbon of an adjacent molecule (Cu2b–C = 3.04 Å). More dramatically, Cu2a is displaced 0.65 Å from the two coordinated nitrogens (Cu2a–N = 2.03 Å) and oxygens (Cu2a–O = 2.26 A) toward the same aromatic ring carbon of the adjacent molecule. The overall geometry of Cu2a is square pyramidal with a Cu2a–C distance of 2.55 Å which suggests a favorable interaction. The molecular structure yields no evidence of thermal electron transfer in the solid state, but the possibility of photoassisted electron transfer cannot be precluded. This structure may represent one conformational form of the mixed-valent species in solution. It further suggests that conformational changes may be the limiting factor in the solution intramolecular electron-transfer rate.

Introduction

The synthesis and characterization of the mixed-valent $Cu^{II}Cu^{I}$–macrocyclic ligand complex **1** were recently reported.



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With two identical Schiff-base ligand coordination sites, it was expected that complex **1** might exhibit facile intramolecular electron transfer. Indeed, the mixed-valent ion, which is stable to disproportionation, exhibits both photoassisted and thermal intramolecular electron transfer, as evidenced by electronic absorption and EPR spectra.[2,3]

Solution EPR spectra are temperature dependent. At the ambient temperature a seven-line spectrum was observed, indicating that the single unpaired electron is interacting with both copper ions. As the solution temperature was lowered, a four-line spectrum was produced, consistent with localization of the electron on a single metal site. From this variable-temperature behavior a value of $1.7 \times 10^{10}\ s^{-1}$ at 298 K was estimated for the thermal intramolecular electron-transfer rate. Unfortunately, solid-state measurements yielded little information since the EPR spectrum of the magnetically nondilute solid consists of only a single line.

Electronic absorption spectra of the mixed-valent species, **1**, are more complex. Several solvent-dependent bands were observed for the complex in the region 600–1700 nm. These absorptions are not present in the precursor $Cu^{II}Cu^{II}$ complex and may be attributable to photoassisted intervalent transfer (eq 1). Mull spectra indicate that similar transitions occur

$$[Cu^{II}Cu^{I}L^{+}] \xrightarrow{h\nu} [Cu^{I}Cu^{II}L^{+}]^* \qquad (1)$$

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[1] On sabbatical leave from the Department of Chemistry, The Johns Hopkins University.

[2] Gagné, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 8367.

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