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Peculiarities of the Complexation of Copper and Silver Adducts of a 3,5-Bis(trifluoromethyl)pyrazolate Ligand with Organoiron Compounds

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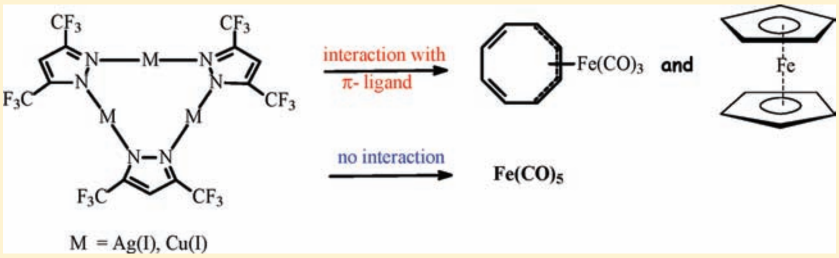
S *Supporting Information*

ABSTRACT:



Interaction of the copper, $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$, and silver, $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$, macrocycles $[3,5\text{-}(CF_3)_2Pz$ = 3,5-bis(trifluoromethyl)pyrazolate] with cyclooctatetraeneiron tricarbonyl, $(cot)Fe(CO)_3$, was investigated by IR and NMR spectroscopy for the first time. The formation of 1:1 complexes was observed at low temperatures in hexane. The composition of the complexes (1:1) and their thermodynamic characteristics in hexane and dichloromethane were determined. The π-electron system of $(cot)Fe(CO)_3$ was proven to be the sole site of coordination in solution and in the solid state. However, according to the single-crystal X-ray data, the complex has a different (2:1) composition featuring the sandwich structure. The complexes of ferrocene with copper and silver macrocycles have a columnar structure (X-ray data).

INTRODUCTION

Cyclic trinuclear complexes of 11 group transition-metal ions are well-known.[1] They represent an important class of coordination compounds used in different fundamental areas, such as acid–base chemistry, metallophilic bonding, supramolecular assemblies, M–M-bonded excimers and exciplexes, and host/guest chemistry.[2,3] The chemistry of copper(I), silver(I), and gold(I) complexes of fluorinated pyrazolate ligands were actively investigated recently.[1a,4] Fluoro substituents usually improve the compound properties such as thermal and oxidative stability.[5] The first contribution to this area concerns the synthesis of $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ and $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ $\{[3,5\text{-}(CF_3)_2Pz]^- =$ 3,5-bis(trifluoromethyl)pyrazolate$\}$.[6] These metal adducts as well as the gold analogues display fascinating luminescent properties.[7] For example, $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ exhibits bright luminescence upon exposure to UV radiation. The emission colors of solid samples and frozen solutions of the trimeric compounds such as $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ show interesting trends with dramatic sensitivities to temperature, solvent, concentration, and excitation wavelengths.[1a,8] The trinuclear metal pyrazolates also exhibit interesting π acid/base properties, which are highly dependent on the pyrazole ring substituents and the metal atom.[8,9] For example, $\{[3,5\text{-}(CH_3)_2Pz]Au\}_3$ is a π base, whereas the fluorinated analogue $\{[3,5\text{-}(CF_3)_2Pz]Au\}_3$ is a π acid.[9] Interaction of some of these compounds with organic bases such as arenes leads to the formation of extended binary stacks.[8,10] Thus, crystals of the $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ adduct with benzene have a sandwich structure, $[(C_6H_6)(\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3)(C_6H_6)]$, according to X-ray data.[10] At the same time, $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ crystallized from a mesitylene/dichloromethane (DCM) solution adopts the $\{(\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3)(Mes)\}_\infty$ columnar structure.[11] Recently, we reported the first example of the interaction between the cyclic trinuclear adducts of copper, $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$, and silver, $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$, and anions ($B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$) in a solvent of low polarity.[12] Two types of complexes were found in solution: $\{[((3,5\text{-}CF_3)_2PzM)_3](B_nH_n)\}^{2-}$ and $\{[((3,5\text{-}CF_3)_2PzM)_3]_2(B_nH_n)\}^{2-}$ ($M = Ag^I$, Cu^I, n = 10, 12).

This paper presents the first study on the complex formation of copper(I) and silver(I) trinuclear metallocycles of 3,5-bis(trifluoromethyl)pyrazolate with neutral organometallic compound cyclooctatetraeneiron tricarbonyl in comparison with iron pentacarbonyl and ferrocene in solution and the solid state.

EXPERIMENTAL SECTION

The macrocycles $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$ and $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ were synthesized according to the published procedure.[13] The solvents,

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Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for 3a, 4a, and 4b

compound	$\{[(\mathrm{cot})\mathrm{Fe(CO)_3}]_2[([3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Ag})_3]\}$ (**3a**)	$\{[\mathrm{Cp_2Fe}]([3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Ag})_3]\}$ (**4a**)	$\{[\mathrm{Cp_2Fe}]([3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Cu})_3]\}$ (**4b**)
molecular formula	$C_{37}H_{19}F_{18}N_6O_6Ag_3Fe_2$	$C_{25}H_{13}F_{18}N_6Ag_3Fe$	$C_{25}H_{13}F_{18}N_6Cu_3Fe$
fw	1420.89	1118.87	985.88
dimens, mm	0.52 × 0.18 × 0.08	0.31 × 0.08 × 0.06	0.24 × 0.12 × 0.08
cryst syst	orthorhombic	triclinic	triclinic
space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a, Å	19.6123(7)	9.438(2)	8.9763(4)
b, Å	12.5957(4)	13.442(3)	9.4659(4)
c, Å	36.643(1)	13.579(3)	19.3435(9)
α, deg	90	82.387(4)	80.863(1)
β, deg	90	87.865(4)	84.951(1)
γ, deg	90	69.191(3)	73.114(1)
V, Å^3	9052.0(5)	1596.2(5)	1551.3(1)
Z	8	2	2
ρ_{calc}, g cm^{-3}	2.085	2.328	2.111
linear absorption (μ), cm^{-1}	20.27	23.95	26.26
$T_{\min}/T_{\max}$	0.468/0.854	0.791/0.839	0.684/0.789
$2\theta_{\max}$, deg	60	56	58
no. of unique reflns (R_{int})	26 167 (0.0605)	8764 (0.0000)	8145 (0.0337)
no. of obsd reflns [$I > 2\sigma(I)$]	21 758	6696	6326
no. of param	1343	506	481
R1 (on F for obsd reflns)[a]	0.0438	0.0486	0.0406
wR2 (on F^2 for all reflns)[b]	0.0831	0.1052	0.0885
GOF	1.051	1.056	1.004

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$.

CH_2Cl_2 and hexane, were dried by reflux over CaH_2 and freshly distilled under an argon atmosphere prior to use. The IR spectra of CH_2Cl_2 and hexane solutions were measured on Infralum FT-801 and Nicolet 6700 FTIR spectrometers in CaF_2 cells (d = 0.12−0.04 cm). IR studies in the ν(CO) region (2100−1900 cm^{-1}) were carried out at various concentrations (10^{-4}−10^{-2} M) and ratios of the reagents. The composition of the complexes in solution was determined by the saturation and continuous-variation (Job's) methods.[14] NMR investigations were carried out on a Bruker Avance 600 spectrometer operating at 600.22 MHz (^{1}H). The temperature was controlled using a Bruker BVT-3000 accessory; the accuracy and stability was ±1 K.

$\{[(\mathrm{cot})\mathrm{Fe(CO)_3}]_2[([3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Ag})_3]\}$ (3a). The macrocycle $\{[3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Ag}\}_3$ (5.73 mg, 0.00615 mmol) was added to a solution of (cot)Fe(CO)$_3$ (1.5 mg, 0.00615 mmol) in CH_2Cl_2/hexane (volume ratio 1:1). Slow solvent evaporation at 5 °C gave crystals. Yield: 70%. Anal. Calcd for $C_{37}H_{19}F_{18}N_6O_6Ag_3Fe_2$: C, 31.2; H, 1.34; N, 5.9. Found: C, 31.4; H, 1.32; N, 5.9.

$\{[\mathrm{Cp_2Fe}]([3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Ag})_3]\}$ (4a) and $\{[\mathrm{Cp_2Fe}]([3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Cu})_3]\}$ (4b). The macrocycle $\{[3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Ag}\}_3$ (5 mg, 0.0054 mmol) or $\{[3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Cu}\}_3$ (4.3 mg, 0.0054 mmol) was added to a solution of Cp_2Fe (1 mg, 0.0054 mmol) in CH_2Cl_2/hexane (volume ratio 1:1). Slow solvent evaporation at 5 °C gave crystals. Yield: 70%. Anal. Calcd for $C_{25}H_{33}F_{18}N_6Ag_3Fe$: C, 26.8; H, 2.95; N, 7.5. Found: C, 26.9; H, 2.85; N, 7.5. Anal. Calcd for $C_{25}H_{33}F_{18}N_6Cu_3Fe$: C, 30.4; H, 3.35; N, 8.5. Found: C, 30.5; H, 3.25; N, 8.4.

X-ray Diffraction Studies of 3a, 4a, and 4b. A single-crystal X-ray diffraction experiment was carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 73 Å, ω-scan technique, T = 100 K). The *APEX II* software[15] was used for collection of frames of data, indexing of reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction and *SHELXTL*[16] for space group and structure determination, refinements, graphics, and structure reporting. The results of the indexing procedure as well as a visual inspection of the three-dimensional and rocking curves of spots have revealed that the crystal of compound **4a** was a twin. All attempts to find an untwinned sample possibly even of smaller dimensions have shown that all crystals have grown as twins with a very small off-orientation angle between twinning components. The collected data set was indexed using *CELL_NOW* software, incorporated in the *APEX II* program package, and then intensities of the collected reflections were described as a superposition of two crystal components with a rotation angle equal to 179.9° along the [0 1 −1] direction. The frames were integrated separately for each component, and then the reflections of two components were separately included in the refinement via HKLF 5 format (BASF is 0.15). All equivalent reflections were merged using the *TWINABS* program. All structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-H atoms. The H (C) atoms were placed geometrically and included in the structure factor calculations in the riding motion approximation. The principal experimental and crystallographic parameters are presented in Table 1.

■ RESULTS AND DISCUSSION

The cyclooctatetraeneiron tricarbonyl, (cot)Fe(CO)$_3$, possesses two potential sites of interaction with Lewis acids: a π-electron system of the cot ligand and CO groups. These two centers could take part in complexation with copper(I) and silver(I) trinuclear metallocycles of 3,5-bis(trifluoromethyl)-pyrazolate known for their affinity to aromatic compounds.

According to the local C_{3v} symmetry of (cot)Fe(CO)$_3$,[17a] there should be two ν(CO) bands in the IR spectra belonging

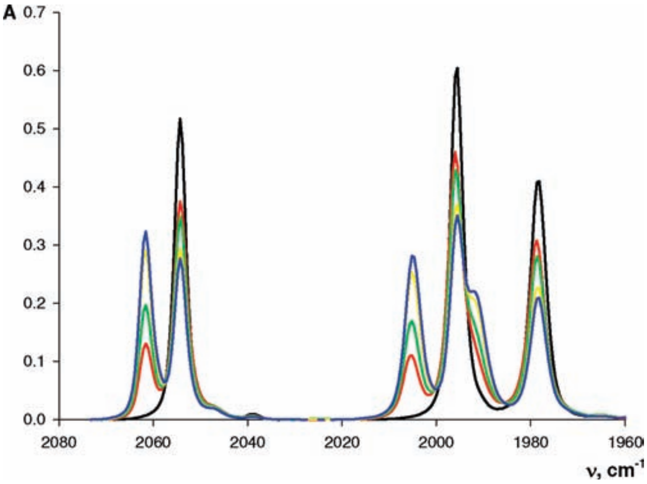

Figure 1. IR spectra in the ν(CO) range of (cot)Fe(CO)$_3$ (0.0015 M, 220 K, black line) and in the presence of {[3,5-(CF$_3$)$_2$Pz]Ag}$_3$ (0.003 M) in hexane at different temperatures: 270 K (red line), 250 K (green line), 230 K (yellow line), and 220 K (blue line). *d* = 0.04 cm.

to A$_1$ vibrations and two degenerate E modes. In fact, three frequencies are observed in the CO stretching region in the solid state and solution[17b] due to the splitting of the degenerate E ν(CO) mode. Thus, three bands at 2054, 1996, and 1979 cm^{-1} of CO stretching vibrations are found in the spectrum of a (cot)Fe(CO)$_3$ solution in hexane at 298 K. Titration of a (cot)Fe(CO)$_3$ solution in hexane with macrocycles {[3,5-(CF$_3$)$_2$Pz]Ag}$_3$ [(LAg)$_3$, **1a**] and {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ [(LCu)$_3$, **1b**; molar ratio from 10:1 to 1:10] has been accompanied by a decrease of the intensity of the initial ν(CO)$^{\text{init}}$ and the appearance of new high-frequency bands. The intensity of these new ν(CO) bands depends on the macrocycle concentration and temperature. The complex formation is preferred at low temperatures (190−250 K) (Figure 1). The complex formation is reversible; the intensity of the free (cot)Fe(CO)$_3$ ν(CO) bands decreases at low temperatures and grows back with increasing temperature.

An increase of the macrocycle concentration (Figure 2) leads to further growth of the new band intensities. As is known, coordination of Bronsted acids at CO groups entails the appearance of new low-frequency bands in the ν(CO) range.[18] Therefore, the absence of low-frequency bands indicates that the CO groups of (cot)Fe(CO)$_3$ do not take part in the complex formation with a macrocyclic Lewis acid. At the same time, new high-frequency ν(CO) bands can be assigned to the CO groups in the complex in which macrocycles interact with the π system of the cyclooctatetraene ligand.

The presence of three bands in the IR spectra of complexes formed between (cot)Fe(CO)$_3$ and macrocycle **1** evidences retention of the CO ligand local symmetry in (cot)Fe(CO)$_3$ upon compexation. The $\Delta\nu$(CO) values are practically equal for complexes of both macrocycles (Table 2). This result corresponds to our previous data[12] concerning the insignificant influence of the 11 group metal atom on the complex stability of **1a** and **1b** with the polyhedral boron hydride anions.

To confirm further the absence of macrocycle interaction with carbonyl ligands, we chose iron pentacarbonyl, possessing only one coordination site: the CO group. No changes were observed in the IR spectra of Fe(CO)$_5$ in hexane at 190−230 K up to 20-fold excess of **1**. Thus, there is no coordination of **1** with Fe(CO)$_5$. In the case of (cot)Fe(CO)$_3$, the spectra (Figures 1 and 2) demonstrate complex formation but without coordination of the CO groups. Therefore, we can conclude the existence of selective interaction with the π-electron system in this case.

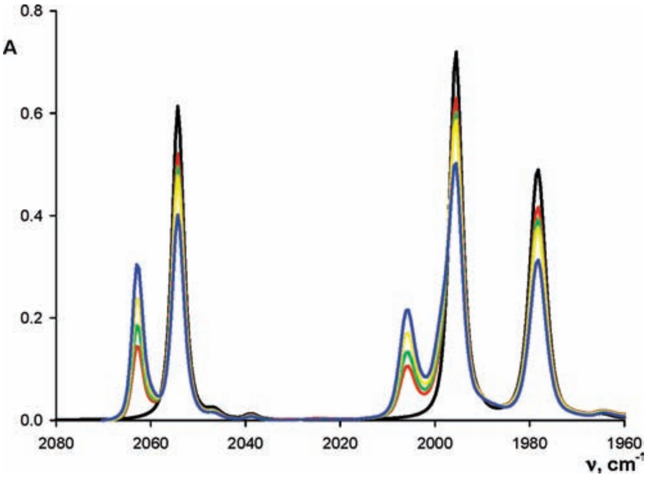

Figure 2. IR spectra in the ν(CO) range of (cot)Fe(CO)$_3$ (0.0015 M, black line) and in the presence of {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ with *c* = 0.00045 M (red line), *c* = 0.00075 M (green line), *c* = 0.001 M (yellow line), and *c* = 0.0015 M (blue line) in hexane. *T* = 210 K; *d* = 0.04 cm.

Table 2. Position of the ν(CO) Bands (in cm^{-1}) of (cot)Fe(CO)$_3$ and Its Complexes with {[3,5-(CF$_3$)$_2$Pz]Ag}$_3$ (2a) and {[3,5-(CF$_3$)$_2$Pz]Cu}$_3$ (2b) at 190 K in Hexane[a]

(cot)Fe(CO)$_3$	**2a**	**2b**
2054	2062 (7)	2061 (8)
1995	2004 (9)	2005 (10)
1978	1990 (12)	1997 (19)

[a] Band shifts given in parentheses are calculated as $\Delta\nu(\text{CO})^{\text{complex}} = \nu(\text{CO})^{\text{complex}} - \nu(\text{CO})^{\text{init}}$.

Another evidence of interaction with the π-electron system comes from the low-temperature ^{1}H NMR measurements of a (cot)Fe(CO)$_3$/**1a** mixture in CD$_2$Cl$_2$. The single resonance of the (cot)Fe(CO)$_3$ protons at 213 K (δ = 5.26 ppm) shifts to high field upon the addition of an equimolar amount of **1a** ($\Delta\delta$ = −0.11 ppm). At the same time, the resonance of **1a** protons (δ = 7.12 ppm) undergoes very small high-field shift to 7.10 ppm. This argues for the formation of a complex between **1a** and the cot ligand of (cot)Fe(CO)$_3$. At room temperature, the changes in the ^{1}H NMR spectra of (cot)Fe(CO)$_3$ upon the addition of a macrocycle are much less pronounced ($\Delta\delta$ = −0.02 ppm). In accordance with these observations, IR spectra of a (cot)Fe(CO)$_3$/**1a** mixture in CH$_2$Cl$_2$ show a very small high-frequency shoulder on the ν(CO)$^{\text{free}}$ band due to the complex formation, which becomes clearly visible below 250 K (see the Supporting Information for details).

For a quantative study of the complex formation, we chose IR spectroscopy in the range of CO group stretching vibrations. The ν(CO) bands are very sensitive for intermolecular interactions.[18b] Hexane was preferred to CH$_2$Cl$_2$, despite the lower solubility of **1** in hexane, because of the higher formation constants of complexes in the last (vide infra), and most important, separation of ν(CO) bands of free (cot)Fe(CO)$_3$ and its complexes.

The compositions of complexes **2a** and **2b** were determined by the saturation and continuous-variation (Job's) methods.[14] It was shown that complexes of only one type are formed in

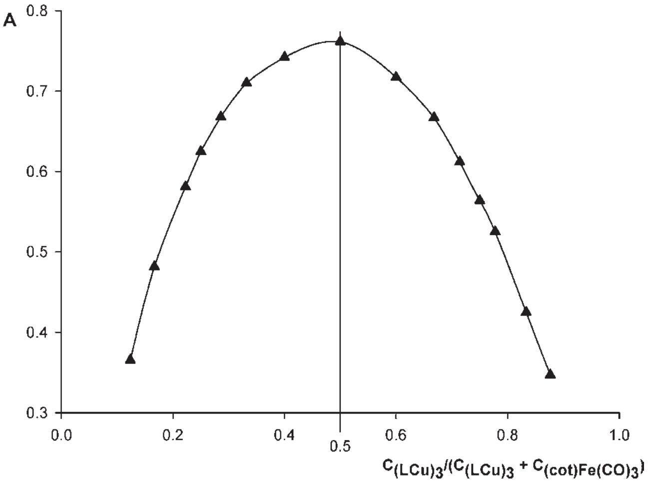

Figure 3. Job's plot: dependence of the band intensity of **2b** (2062 cm^{-1}) on the composition of the isomolar solution of (cot)Fe-$(CO)_3$ and **1b**.

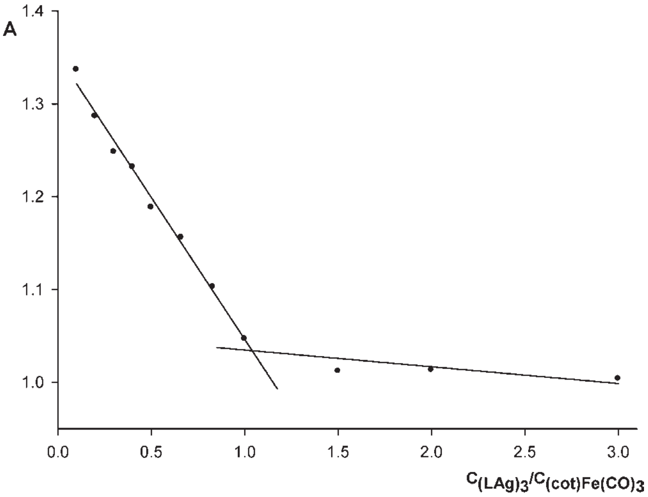

Figure 4. Saturation plot: dependence of the band intensity of (cot)$Fe(CO)_3$ (2054 cm^{-1}) on the **1a** concentration change.

solution. The formation of complexes, which contain one molecule of (cot)$Fe(CO)_3$ per one molecule of the macrocycle, occurs at the molar ratio of (cot)$Fe(CO)_3$/**1** from 10:1 to 1:10. Thus, they can be formulated as $\{[(cot)Fe(CO)_3][(LAg)_3]\}$ (**2a**) and $\{[(cot)Fe(CO)_3][(LCu)_3]\}$ (**2b**), respectively (Figures 3 and 4).

Quantitative analysis of the spectra allowed calculation of the formation constants for complexes **2a** and **2b** at different temperatures and then of the thermodynamic parameters. For **2a**, the enthalpy value, $\Delta H^{\circ\text{hexane}}$, is -4.7 ± 0.2 kcal mol^{-1} and the entropy value, $\Delta S^{\circ\text{hexane}}$, is -9 ± 1 cal mol^{-1} K^{-1}, and for **2b**, $\Delta H^{\circ\text{hexane}} = -5.9 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\circ\text{hexane}} = -17 \pm 2$ cal mol^{-1} K^{-1}. The thermodynamic characteristics indicate that interaction of **1a** with (cot)$Fe(CO)_3$ is slightly weaker than that of **1b**, as was found for the complex formation of macrocycles with polyhedral boron hydride anions.[12] The formation of **2a** and **2b** was suppressed upon a change in the solvent from the nonpolar hexane to the midpolar CH_2Cl_2 because of a decrease of the formation constants by 2 orders of magnitude (for **2a**, formation constant values at 190 K are $K_f^{\text{hexane}} = (2.7 \pm 0.2) \times 10^3$ and $K_f^{CH_2Cl_2} = (3.1 \pm 0.2) \times 10^1$ L mol^{-1}). The formation enthalpies of **2a** are also lower in DCM than in hexane ($\Delta H^{\circ CH_2Cl_2} = -3.8 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\circ CH_2Cl_2} = -13 \pm 2$ cal mol^{-1} K^{-1}), and the same goes for **2b** ($\Delta H^{\circ CH_2Cl_2} = -4.7 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\circ CH_2Cl_2} = -18 \pm 3$ cal mol^{-1} K^{-1}) .

Table 3. Selected Bond Lengths (Å) in 3a

	adduct A	adduct B
Ag1−C22	2.875(6)	3.368(6)
Ag1−C23	3.053(6)	3.000(6)
Ag1−C27	3.305(6)	3.375(6)
Ag1−C28	3.594(6)	3.274(6)
Ag1−C34	3.380(6)	3.543(6)
Ag2−C20	3.013(5)	3.321(6)
Ag2−C21	2.912(6)	2.801(6)
Ag2−C22	3.734(6)	3.155(6)
Ag3−C32	3.048(6)	3.028(6)
Ag3−C33	2.908(6)	3.125(6)

The complex of (cot)$FeCO_3$ with macrocycle **1a** was isolated in the solid state by the treatment of **1a** with an equimolar amount of (cot)$FeCO_3$ in a CH_2Cl_2/hexane solution. According to elemental analysis and single-crystal X-ray diffraction data, it has a 2:1 composition, i.e., contains two molecules of (cot)$Fe(CO)_3$ per one molecule of **1a**, and can be formulated as $\{[(cot)Fe(CO)_3]_2[(LAg)_3]\}$ (**3a**). There are two independent crystallographic adducts (A and B, Table 3) in the **3a** crystal, having similar structure with small differences in the Ag···C contact lengths. The molecular structure of one of them is shown in Figure 5.

In **3a**, two molecules of (cot)$Fe(CO)_3$ are located at two sides of the macrocycle plane in the same manner as that in the sandwich complex of **1a** with benzene, $\{(C_6H_6)(\mathbf{1a})(C_6H_6)\}$.[10] One (cot)$Fe(CO)_3$ molecule is bonded with two Ag atoms and another one only with the third Ag atom. Ag atoms of the macrocycle are coordinated to the butadiene fragment of the cot ligand, which is not involved in interaction with the Fe atom. The structure of **3a** is characterized by multiple Ag···C contacts (Table 3), which are well below the sum of the van der Waals radii for Ag and C (1.72 Å for Ag and 1.70 Å for C).[19] It is notable that interaction of the one (cot)$Fe(CO)_3$ molecule with the macrocycle takes place by C atoms of the formally double C═C bonds, while the second (cot)$Fe(CO)_3$ molecule is bonded by C atoms of the single C−C bond. The average Ag···C distance (3.06 Å) is shorter than that in complexes of **1a** with benzene (3.11 Å) and mesitylene (3.25 Å).[10] Short C···N and C···C contacts between the cot ligand and one of the pyrazole rings of **1a** are also observed [3.169(6)−3.459(7) Å]. In agreement with the IR spectroscopic data in solution, the CO groups of (cot)$Fe(CO)_3$ do not take part in interaction with the macrocycle [the shortest Ag···O distance is 3.320(6) Å].

The dihedral angle between the planes of two butadiene fragments of the cot ligands in **3a** is 44.5° (av) and slightly differs from that for pure (cot)$Fe(CO)_3$ (46.2°).[20] The Fe−C-(cot) distances in **3a** [2.05 and 2.19 Å (av) for internal and external C atoms of the butadiene fragment] do not change at the complex formation relative to those in pure (cot)$Fe(CO)_3$ (2.05 and 2.18 Å, respectively).[20] Similarly, no changes are observed for the Fe−CO distance [1.80 Å for free (cot)$Fe(CO)_3$[20] and 1.79 Å (av) for **3a**]. Thus, coordination with the macrocycle does not lead to appreciable changes of the (cot)$Fe(CO)_3$ symmetry.

IR spectra of **3a** in the solid state (as a Nujol mull; Figure 6) show three new high-frequency ν(CO) bands (2061, 2013, and

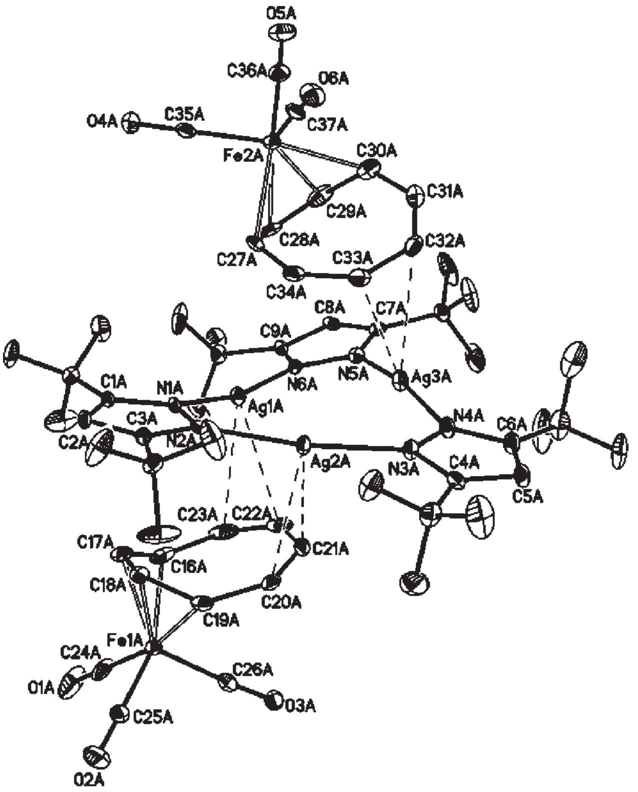

Figure 5. Molecular structure of one of the two independent $\{[(\mathrm{cot})\mathrm{Fe(CO)_3}]_2[(\mathrm{LAg})_3]\}$ adducts with thermal ellipsoids drawn at the 30% probability level (H atoms are omitted for clarity). Dashed lines show the shortest Ag···C distances.

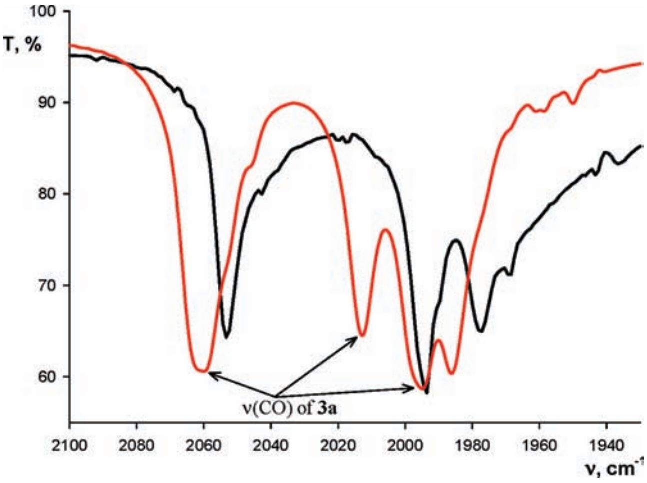

Figure 6. IR spectra of $(\mathrm{cot})\mathrm{Fe(CO)_3}$ (black line) and $\{[(\mathrm{cot})\mathrm{Fe(CO)_3}]_2[(\mathrm{LAg})_3]\}$ (red line) in the solid state, as a Nujol mull.

1995 cm^{-1}). This confirms participation of the π-aromatic ligand of $(\mathrm{cot})\mathrm{Fe(CO)_3}$ in interaction with the macrocycle, in agreement with the X-ray data and spectral changes in solution. Upon dissolution of complex **3a** in hexane, partial dissociation is observed and free ν(CO) bands of $(\mathrm{cot})\mathrm{Fe(CO)_3}$ appear in accordance with the formation constant values.

Basing on our results on interaction of macrocycles with $(\mathrm{cot})\mathrm{Fe(CO)_3}$ and published data[11] on the columnar structure of $\{(\{[3,5\text{-}(\mathrm{CF_3})_2\mathrm{Pz}]\mathrm{Ag}\}_3)(\mathrm{Mes})\}_\infty$, we chose metallocenes in order to get binary stacks with organometallic compounds. Indeed, the X-ray diffraction study of the complexes $\{[\mathrm{Cp_2Fe}]([\mathrm{LAg}]_3]\}$ (**4a**) and $\{[\mathrm{Cp_2Fe}]([\mathrm{LCu}]_3]\}$ (**4b**) showed that in the solid state these compounds form binary stacks (1:1) (Figures 7 and 8 and Table 4).

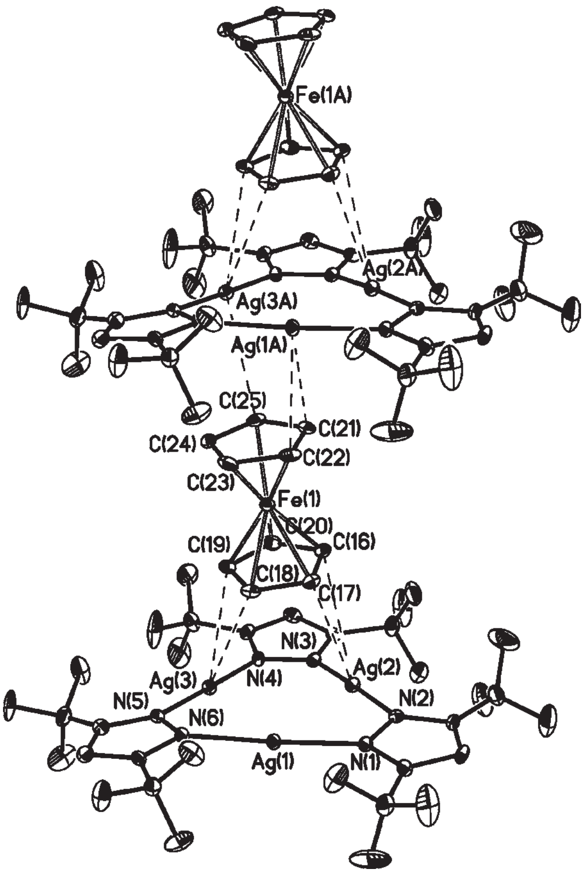

Figure 7. Molecular structure of $\{[\mathrm{Cp_2Fe}]([\mathrm{LAg}]_3]\}$ with thermal ellipsoids drawn at the 30% probability level (H atoms are omitted for clarity).

In these complexes, ferrocene molecules alternate with macrocycle molecules and are related to each other via the shortest M···C contacts. The structures of binary stacks in the crystals of **4a** and **4b** are very similar including a number of shortened contacts and their values [Ag···C 2.982(7)−3.278(7) Å for **4a**; Cu···C 2.939(4)−3.160(4) Å for **4b**]. In the copper(I) complexes with η^2 binding of arenes, the observed Cu···C(π) contacts are usually shorter [2.129(6)−2.414(6),[21a] 2.271(2)−2.455(3),[21b] and 2.507(2)−2.910(4) Å].[21c] On the other hand, the lengths of the M···C(π) contacts in **4a** and **4b** are close to those observed for a double-sandwich silver(I) polymer with 1,1′-bis(diethyldithiocarbamate)ferrocene, where the metal is bridging two ferrocene fragments[22] [2.972(8) and 3.027(8) Å]. In both **4a** and **4b**, the ferrocene molecule is slightly inclined to the plane of the macrocycle (the inclination angle defined as the angle between the ferrocene axis, passing through the Cp centers and Fe atom, and the average plane of the macrocycle, passing through the metal atoms, are 84.6° and 82.4° for **4a** and **4b**, respectively). In addition of the shortened contact with Cu or Ag atoms, each of the Cp ligands forms shortened contacts with the N atoms of one of the pyrazole fragments of the neighboring macrocycle [C···N 3.233(9)−3.370(9) Å for **4a**; 3.198(5)−3.279(5) Å for **4b**]. It is significant that the previously described

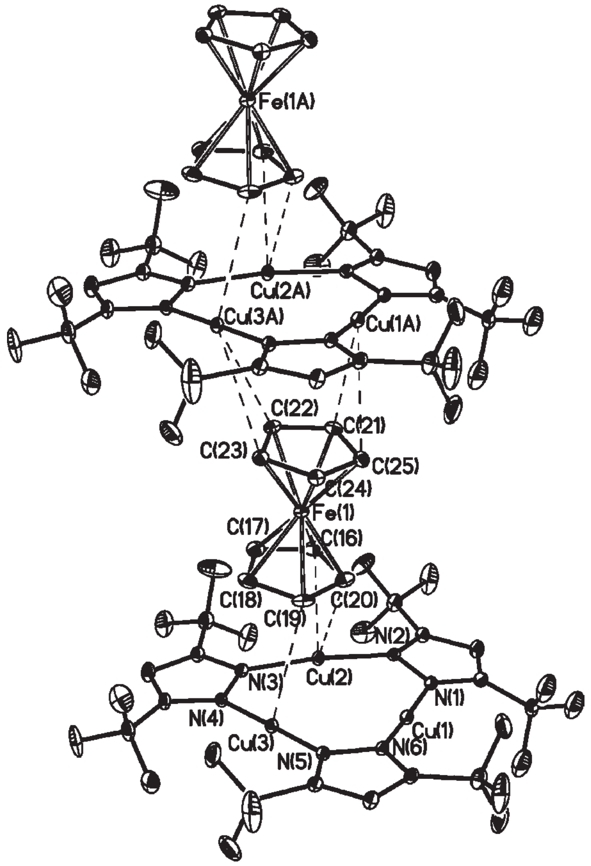

Figure 8. Molecular structure of $\{[Cp_2Fe](LCu)_3]\}$ with thermal ellipsoids drawn at the 30% probability level (H atoms are omitted for clarity).

Table 4. Selected Bond Lengths (Å) in Complexes 4a and 4b

4a		4b	
Ag2A−C21	3.121(6)	Cu1A−C21	2.942(4)
Ag2A−C22	2.998(7)	Cu1A−C25	3.160(4)
Ag1−C16	3.275(6)	Cu2−C16	2.939(4)
Ag1−C17	3.049(6)	Cu2−C20	3.067(4)
Ag3−C18	3.110(7)	Cu3−C19	3.042(4)
Ag3−C19	2.982(7)	Cu3A−C22	3.154(4)
Ag3A−C25	3.074(6)	Cu3A−C23	3.151(4)

complex of a mercury trinuclear macrocycle with ferrocene $\{[(o\text{-}C_6F_4Hg)_3]_2(Cp_2Fe)\}$,[23] which is in contact with complexes **4a** and **4b**, has a sandwich structure.

CONCLUSIONS

The IR spectroscopic study on the complex formation of the copper, $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$, and silver, $\{[3,5\text{-}(CF_3)_2Pz]Ag\}_3$, macrocycles $[3,5\text{-}(CF_3)_2Pz = 3,5\text{-bis(trifluoromethyl)pyrazolate}]$ with $(cot)Fe(CO)_3$ combined with single-crystal X-ray analysis shows selectivity of the interaction. Complexes formed both in the solid state and in solution feature the same site of coordination: π-electron system of the cyclooctatetraene ligand. Both macrocycles **1a** and **1b** do not interact with carbonyl groups, as additionally confirmed by measurements on the **1**/$Fe(CO)_5$ mixtures. Interestingly, complexes of **1** with $(cot)Fe(CO)_3$ have different compositions in solution and in the solid state (1:1 and 2:1, respectively). According to X-ray data, complex **3a** has a sandwich structure. The enthalpy values determined in solution are characteristic for weak complexes. Their formation constants are 2 orders of magnitude lower than the formation constants determined previously for complexes with polyhedral boron hydride anions.[12] Ferrocene interaction with macrocycles leads to formation complexes with columnar structure according to X-ray data. The results obtained show for the first time that the affinity of macrocycles **1a** and **1b** to the aromatic compounds is retained in their interaction with organoiron complexes bearing π-aromatic ligands.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** IR and NMR spectra of $(cot)Fe(CO)_3$ in the presence of macrocycles in hexane and DCM and crystallographic information in CIF format for the complexes $\{[(cot)Fe(CO)_3]_2[(LAg)_3]\}$, $\{[Cp_2Fe]([LAg)_3]\}$, and $\{[Cp_2Fe]([LCu)_3]\}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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