

δ 156.3 (s, C₁), 128.7 (dd, J_{CH} = 159, C_o), 127.2 (br d, J_{CH} = 164, C_m), 123.5 (br d, J_{CH} = 162, C_p), 71.5 (t, J_{CH} = 145, CH₂O), 63.5 (br q, J_{CH} = 139, MeO). The elemental analyses of **1e** were variable, we presume, because DME is labile. The analogous triflate derivative (see below) analyzed consistently.

Mo(NPh)₂(OSO₂CF₃)₂(DME). Mo(NPh)₂Cl₂(DME) (1.00 g, 2.3 mmol) was dissolved in 40 mL of diethyl ether and the solution was chilled to -20 °C. Silver trifluoromethanesulfonate (1.17 g, 4.6 mmol) was added in small solid portions, and a precipitate of silver chloride formed. The reaction was allowed to warm to room temperature and was stirred overnight. The silver chloride was removed by filtration and washed with DME. The solvents were removed from the filtrate in vacuo, and the residue was recrystallized from dichloromethane layered with pentane; yield (1.27 g, 84%). This reaction may also be run in DME as the solvent. ¹H NMR (CD₂Cl₂): δ 7.45–7.20 (m, 10, H_{ar}), 4.08 (s, 6, MeO), 4.04 (s, 4, CH₂O). ¹³C NMR (CD₂Cl₂): δ 156.9 (s, C₁), 130.2 (d, J_{CH} = 139, C_o), 128.9 (d, J_{CH} = 144, C_m), 125.9 (d, J_{CH} = 165, C_p), 72.2 (t, J_{CH} = 148, CH₂O), 65.4 (q, J_{CH} = 144, MeO). ¹⁹F NMR (CD₂Cl₂): δ 29.5 (s). Anal. Calcd for MoC₁₈H₂₀F₆Cl₂N₂O₈S₂: C, 32.44; H, 3.02; N, 4.20. Found: C, 32.31; H, 3.01; N, 4.13.

Mo(N-*t*-Bu)₂Cl₂(DME) (1f). Chlorotrimethylsilane (8.91 g, 0.082 mol, 28 equiv) was added dropwise to a solution of *tert*-butylamine (3.43 g, 0.047 mol, 16 equiv) in DME (60 mL). A white precipitate formed. To this slurry was added ammonium dimolybdate (1 g, 2.94 mmol) all at once as a solid. The mixture was heated to 65 °C for 5 h. The mixture was then filtered. The solvent was removed from the orange-brown filtrate to give a brown residue. The brown residue was extracted with pentane to give a yellow solution, from which the solvent was removed in vacuo to give Mo(N-*t*-Bu)₂Cl₂(DME) as a yellow powder which is >95% pure by ¹H NMR; yield 1.35 g (58%). Recrystallization from pentane yields analytically pure yellow needles. ¹H NMR: δ 3.46 (s, 6, MeO), 3.24 (s, 4, CH₂O), 1.40 (s, 18, CMe₃). ¹³C NMR: δ 71.7 (s, CMe₃), 70.7 (q, CH₂O), 62.4 (d, CH₂O), 30.1 (q, CMe₃). Anal. Calcd for MoC₁₂H₂₈N₂Cl₂O₂: C, 36.10; H, 7.07; N, 7.02. Found: C, 35.87; H, 7.13; N, 6.76.

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Crystal Structure and Infrared and NMR Spectra of $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$: A Two-Dimensional Extended Structure Due to Sodium–Isocarbonyl Interactions

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Introduction

Transition-metal carbonylate anions are of great importance in organometallic chemistry.¹ Solid-state structures of metal carbonylate anions are usually determined by X-ray analyses with large counterions (e.g., [PPN]⁺, [PPh₄]⁺), the anions and cations being well separated in crystal lattices. With alkali-metal, alkaline-earth-metal aluminum,² and lanthanide cations,³ interactions between these cations and the carbonyl oxygen atoms of the metal carbonylates (i.e. isocarbonyl linkages) have been observed

Table I. Crystallographic Data for $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$

chem formula	C ₄₈ H ₄₀ Fe ₂ N ₈ ·Na ₂ O ₈	Z	4
fw	1014.58	<i>d</i> (calc), g cm ⁻³	1.346
space group	<i>Pbca</i> (No. 61)	temp, °C	-60
<i>a</i> , Å	15.796 (4)	radiation (λ, Å)	Mo Kα (0.710 73)
<i>b</i> , Å	17.203 (6)	μ, cm ⁻¹	6.512
<i>c</i> , Å	18.428 (4)	<i>R</i> (F _o)	0.057
<i>V</i> , Å ³	5007.3	<i>R</i> _w (F _o)	0.045

in solution as well as in the solid state, giving rise to contact ion pairs. Ion-pairing phenomena are most conveniently studied in solution by infrared spectroscopy and in the solid state by single-crystal X-ray analyses.²

The solid-state structures of the sodium and potassium salts of the typical mononuclear carbonylate anions [Fe(CO)₄]²⁻ have been determined.⁴ They reveal interesting interactions between [Fe(CO)₄]²⁻ and Na⁺ or K⁺. The structure of the typical dinuclear dianion [Fe₂(CO)₈]²⁻ has previously been determined as its [PPN]⁺ and [PPh₄]⁺ salts.⁵ In view of the interesting structural aspects of the ion-pairing phenomena in the solid state,² we set out to determine the structure of Na₂[Fe₂(CO)₈]. Na₂[Fe₂(CO)₈] crystallizes in saturated pyridine solutions as the title compound. Reported herein is the novel two-dimensional extended sheetlike structure of $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$ as determined by X-ray analysis and related NMR and infrared studies. The crystal structure of $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$ is to our knowledge the first example of a dinuclear transition-metal carbonylate dianion involved in an extended structure via isocarbonyl linkages.⁶

Experimental Section

All manipulations were carried out on a standard high-vacuum line or in a drybox under an atmosphere of dry, pure N₂. Tetrahydrofuran (THF) was dried by distillation from sodium–benzophenone ketyl into storage bulbs equipped with Teflon stopcocks and containing sodium–benzophenone ketyl. CH₃CN was dried over P₄O₁₀ with continuous stirring for 2–3 days followed by distillation into storage bulbs. Pyridine was dried over sodium and distilled prior to use. Na₂[Fe₂(CO)₈] and [PPh₄]₂[Fe₂(CO)₈] were prepared by procedures reported in the literature.^{5b}

All IR spectra were recorded with 2-cm⁻¹ resolution using a Mattson-Polaris FT-IR spectrometer. Solution spectra were obtained in Perkin-Elmer liquid cells with 0.1-mm Teflon spacers and KBr windows. Spectra in Nujol mull were obtained with KBr plates. Proton NMR (δ (TMS) = 0.00 ppm) and ¹³C NMR (δ (TMS) = 0.00 ppm) spectra were obtained on a Bruker AM-250 NMR spectrometer operating at 250.14 and 101.25 MHz, respectively.

Preparation of $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$. In the drybox 500 mg of Na₂[Fe₂(CO)₈] was dissolved in a minimal amount of dry pyridine and the resulting solution was filtered and stored at -40 °C for 1 week, during which time red crystals of $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$ bigger than 2 × 2 × 2 mm³ were obtained.

Infrared Spectra. For $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$ (ν_{CO} , cm⁻¹): in Nujol mull 1927 (m), 1855 (m, sh), 1830 (s); in THF 1986 (w), 1970 (vw), 1922 (s), 1875 (s), 1829 (m); in CH₃CN 1977 (w), 1939 (w), 1914 (s), 1863 (s), 1840 (w, sh); in pyridine 1973 (w), 1942 (w, sh), 1914 (m), 1863 (s), 1940 (w, sh). For [PPh₄]₂[Fe₂(CO)₈] (ν_{CO} , cm⁻¹): in Nujol mull 1909 (m), 1847 (s, br); in CH₃CN^{5b} 1992 (vw), 1953 (w, sh), 1914 (m), 1865 (s).

¹³C{¹H} NMR Spectra. For $\{[(\text{C}_5\text{H}_5\text{N})_4\text{Na}]_2[\text{Fe}_2(\text{CO})_8]\}_n$ (THF-*d*₈, 303 K, ppm): δ 227.84 (s, carbonyls); δ 150.74 (s), δ 136.24 (s), δ 124.29 (s, pyridines).

X-ray Crystal Structure Determination. A crystal of the size 0.45 × 0.50 × 0.60 mm³ was cut from a bigger crystal, coated with epoxy resin, and then mounted on the tip of a glass fiber under N₂. All crystallographic data were collected at -60 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by a least-squares refinement of the angular

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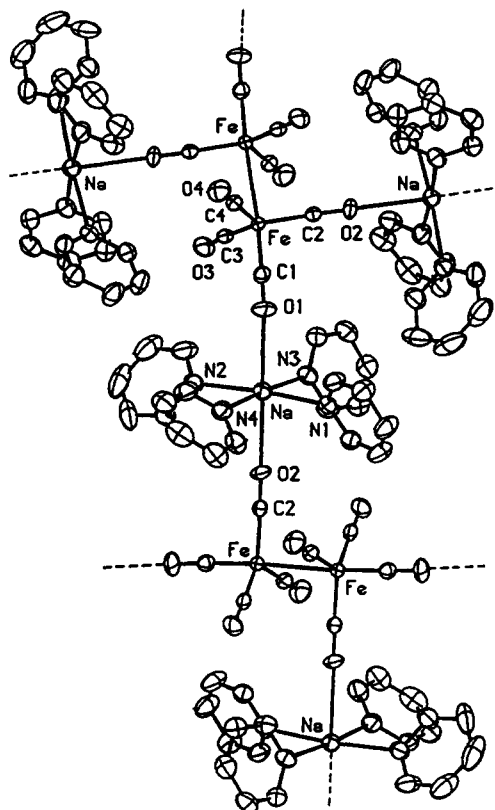


Figure 1. ORTEP drawing of a portion of the two-dimensional structure of $\{[(C_5H_5N)_4Na]_2[Fe_2(CO)_8]\}_n$ (30% thermal ellipsoids). Hydrogen atoms are omitted.

settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range 24–30°. The diffraction symmetry (D_{2h} , mmm) and the systematic absences ($hk0$ for $k = 2n + 1$; $h0l$ for $h = 2n + 1$; $0kl$ for $l = 2n + 1$) uniquely determine the space group $Pcab$ (No. 61). The data set was transformed to the standard space group $Pbca$. Crystallographic data are given in Table I.

All data were corrected for Lorentz and polarization effects. Decay (0.2%) and absorption effects (absorption coefficient = 6.512 cm^{-1}) were not corrected for. The structure was solved by employing a combination of MULTAN 11/82 and difference Fourier techniques with analytical scattering factors used throughout the structure refinement and both real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms. All the crystallographic computations were carried out on a DEC Vax station 3100 computer, using the Structure Determination Package (SDP).⁷ After all of the non-hydrogen atoms were located and refined, the hydrogen atoms of the pyridines were placed at calculated positions ($C-H = 0.95 \text{ \AA}$, $B(H) = 1.3B(C) \text{ \AA}^2$). Then, with the positional and thermal parameters of all of the hydrogens fixed, the non-hydrogen atoms were refined anisotropically. New hydrogen positions were calculated again, and this procedure was repeated until the parameters of non-hydrogen atoms were refined to convergence (final shift/error ≤ 0.03). $R_F = 0.057$, $R_{wF} = 0.045$, and $GOF = 1.26$ with 307 variables refined for 2388 unique observations [$I \geq 1.0\sigma(I)$] of 2839 reflections collected over the 2θ range $4^\circ \leq 2\theta \leq 45^\circ$. The highest residual peak on the final difference Fourier map is 0.37 e \AA^{-3} .

Results

Carbonyl stretching frequencies of $\{[(C_5H_5N)_4Na]_2[Fe_2(CO)_8]\}_n$ in different media and its ^{13}C NMR chemical shift are given in the Experimental Section. The crystal structure of $\{[(C_5H_5N)_4Na]_2[Fe_2(CO)_8]\}_n$ consists of puckered polymeric sheets stacked along the crystallographic b axis. There are no abnormal interactions between the sheets. The two-dimensional sheetlike network is formed by the interactions between the Na^+ cations and the carbonyl oxygen atoms of the $[Fe_2(CO)_8]^{2-}$ dianion (i.e., Na -isocarbonyl linkages). Figure 1 shows a portion of the

Table II. Non-Hydrogen Positional Parameters for $\{[(C_5H_5N)_4Na]_2[Fe_2(CO)_8]\}_n$

atom	x	y	z	$B, \text{\AA}^2$ ^a
Fe	0.55776 (3)	0.02757 (3)	0.05000 (3)	2.54 (1)
Na	0.74119 (9)	-0.05218 (9)	-0.2127 (1)	3.66 (4)
O1	0.6702 (2)	0.0825 (2)	0.1646 (2)	4.77 (7)
O2	0.6536 (1)	-0.0188 (2)	-0.0902 (2)	4.20 (7)
O3	0.5054 (2)	-0.0948 (2)	0.1639 (2)	4.54 (7)
O4	0.4841 (2)	0.1792 (2)	0.0439 (2)	5.20 (8)
N1	0.6375 (2)	-0.1155 (2)	-0.2824 (2)	3.78 (8)
N2	0.8418 (2)	0.0007 (2)	-0.1299 (2)	4.41 (9)
N3	0.7138 (2)	0.0706 (2)	-0.2873 (2)	4.20 (9)
N4	0.7582 (2)	-0.1784 (2)	-0.1394 (2)	4.37 (9)
C1	0.6249 (2)	0.0605 (3)	0.1182 (3)	3.20 (9)
C2	0.6142 (2)	-0.0011 (2)	-0.0360 (2)	2.96 (9)
C3	0.5236 (2)	-0.0470 (3)	0.1172 (3)	3.19 (9)
C4	0.5115 (2)	0.1183 (3)	0.0444 (3)	3.30 (9)
C11	0.5685 (2)	-0.1036 (3)	-0.2609 (3)	4.7 (1)
C12	0.5119 (3)	-0.1514 (3)	-0.2853 (3)	5.9 (1)
C13	0.5276 (3)	-0.2142 (3)	-0.3358 (4)	6.1 (1)
C14	0.5981 (3)	-0.2280 (3)	-0.3585 (3)	5.5 (1)
C15	0.6501 (2)	-0.1774 (3)	-0.3308 (3)	4.5 (1)
C21	0.8395 (3)	-0.0056 (3)	-0.0459 (3)	5.3 (1)
C22	0.8892 (3)	0.0284 (4)	0.0062 (4)	8.0 (2)
C23	0.9444 (3)	0.0716 (4)	-0.0283 (4)	9.0 (2)
C24	0.9475 (3)	0.0779 (4)	-0.1146 (5)	8.6 (2)
C25	0.8951 (3)	0.0423 (3)	-0.1617 (3)	6.2 (1)
C31	0.7486 (2)	0.1027 (3)	-0.3530 (3)	4.4 (1)
C32	0.7241 (3)	0.1661 (3)	-0.3967 (3)	5.2 (1)
C33	0.6599 (3)	0.2006 (3)	-0.3712 (3)	5.2 (1)
C34	0.6235 (3)	0.1685 (3)	-0.3044 (3)	5.0 (1)
C35	0.6521 (3)	0.1048 (3)	-0.2650 (3)	5.1 (1)
C41	0.7009 (3)	-0.2193 (3)	-0.1139 (3)	5.0 (1)
C42	0.7038 (3)	-0.2899 (3)	-0.0728 (3)	5.9 (1)
C43	0.7701 (3)	-0.3209 (3)	-0.0584 (4)	6.4 (1)
C44	0.8306 (3)	-0.2819 (3)	-0.0826 (3)	6.4 (1)
C45	0.8225 (3)	-0.2098 (3)	-0.1221 (3)	5.6 (1)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,2) + bc(\cos \alpha)\beta(2,3)]$.

Table III. Selected Bond Distances (Å) and Angles (deg) for $\{[(C_5H_5N)_4Na]_2[Fe_2(CO)_8]\}_n$

Bond Distances			
Fe-Fe	2.815 (1)	Na-N1	2.458 (4)
Fe-C1	1.736 (4)	Na-N2	2.445 (4)
Fe-C2	1.780 (4)	Na-N3	2.471 (4)
Fe-C3	1.780 (5)	Na-N4	2.481 (4)
Fe-C4	1.781 (5)	O1-C1	1.173 (4)
Na-O1	2.587 (3)	O2-C2	1.164 (4)
Na-O2	2.585 (3)	O3-C3	1.154 (4)
		O4-C4	1.163 (4)
Bond Angles			
Fe-Fe-C1	175.7 (1)	O2-Na-N1	87.0 (1)
Fe-Fe-C2	85.4 (1)	O2-Na-N2	89.4 (1)
Fe-Fe-C3	79.9 (1)	O2-Na-N3	92.3 (1)
Fe-Fe-C4	84.6 (1)	O2-Na-N4	85.6 (1)
C1-Fe-C2	98.5 (2)	N1-Na-N2	173.4 (1)
C1-Fe-C3	96.7 (2)	N1-Na-N3	90.4 (1)
C1-Fe-C4	94.9 (2)	N1-Na-N4	85.4 (1)
C2-Fe-C3	117.5 (2)	N2-Na-N3	95.3 (1)
C2-Fe-C4	119.0 (2)	N2-Na-N4	88.8 (1)
C3-Fe-C4	119.5 (2)	N3-Na-N4	175.3 (1)
O1-N-O2	178.8 (1)	Na-O1-C1	148.4 (3)
O1-Na-N1	93.8 (1)	Na-O2-C2	177.6 (3)
O1-Na-N2	89.8 (1)	Fe-C1-O1	179.7 (9)
O1-Na-N3	86.8 (1)	Fe-C2-O2	177.2 (3)
O1-Na-N4	95.4 (1)	Fe-C3-O3	175.6 (3)
		Fe-C4-O4	176.2 (4)

network. Crystal data, positional parameters, and important bond distances and angles are listed in Tables I–III, respectively. A center of symmetry resides at the midpoint of the Fe–Fe bond; therefore only half the formula of $\{[(C_5H_5N)_4Na]_2[Fe_2(CO)_8]\}_n$ is crystallographically independent. Four carbonyl groups (two axial and two equatorial carbonyls) in each $[Fe_2(CO)_8]^{2-}$ unit are

(7) SDP (developed by B. A. Frenz and Associates, Inc., College Station, TX 77840) was used to process X-ray data, to apply corrections, and to solve and refine the structures.

connected to four different Na⁺ cations via isocarbonyl linkages. Na⁺ is in a tetragonally distorted octahedral environment, with four pyridine ligands arranged in a propeller fashion in the equatorial plane and two oxygen atoms (one from an axial carbonyl C1O1 of a [Fe₂(CO)₈]²⁻ unit, the other from an equatorial carbonyl C2O2 of a different [Fe₂(CO)₈]²⁻ unit) in the axial positions.

Discussion

Structure. In general, coordination of the oxygen atoms of metal carbonyls to 2+ and 3+ cations causes a decrease in the M-C bond distance and an increase in the C-O bond distance.^{2,3e,j,8,9} In the title compound, however, the structure of the dianion does not seem to be perturbed by the Na-isocarbonyl interactions. For example, all the equatorial Fe-C and C-O bond distances are the same within experimental error, irrespective of whether they participate in isocarbonyl linkages. The geometry of [Fe₂(CO)₈]²⁻ is only slightly distorted from ideal D_{3d} symmetry, thereby implying a weak ion-pairing effect. The structural parameters of [Fe₂(CO)₈]²⁻ in the title compound are very similar to those of previously determined [Fe₂(CO)₈]²⁻ structures.⁵ The Fe-Fe bond distance of 2.815 (1) Å in the title compound is not significantly longer than the values in [PPN]₂[Fe₂(CO)₈] (2.787 (2) Å)^{5a} and in [PPh₄]₂[Fe₂(CO)₈] (2.792 (1) Å).^{5b}

The coordination of pyridines in a "propeller assemblage" around Na⁺ in the title compound resembles that observed in (C₅H₅)₄Yb(BH₄)₂¹⁰ and in [(C₅H₅)₄Mg][Mo(CO)₃CP]₂.⁹ The arrangement of five pyridine ligands in an equatorial plane of pentagonal-bipyramidal geometry is also observed for Yb²⁺ in [Yb(C₅H₅)₅(CH₃CN)₂][Hg[Fe(CO)₄]₂].¹¹ The Na-N distances in the title compound have an average of 2.464 Å. The Na-N distances of 2.463 (5)^{12d} and 2.471 (7) Å^{12a} for six-coordinate Na⁺ cations are comparable to the value reported here. The Na-N distances for four- and five-coordinate Na⁺ cations are 2.391 (5)^{12b} and 2.384 (6) Å,^{12c} respectively.

Two Na-O distances of 2.587 (3) and 2.585 (3) Å in the title compound are quite long compared to other Na-O distances observed in the interactions between Na⁺ and isocarbonyls, which range from 2.318 to 2.555 Å.^{4a,13} The Na-O1-C1 and the Na-O2-C2 angles are 148.4 (3) and 177.6 (3)°, respectively. Na-O-C angles involving terminal carbonyls in the other reported structures range from 115.1 to 162.4°.¹³ On the basis of the large range of Na-O-C angles observed, we believe that the M-O-C angles are not critical for effective cation-isocarbonyl interactions and that steric effects in the solid state control the angularity of these interactions.

Infrared and NMR Spectra. The infrared spectrum of {[C₅H₅N]₄Na₂[Fe₂(CO)₈]}_∞ in Nujol mull shows three infrared absorptions at 1927 (m), 1855 (m, sh), and 1830 (s) cm⁻¹. On the other hand, only two major carbonyl absorptions are observed for [PPh₄]₂[Fe₂(CO)₈] both in Nujol mull (1909 (m), 1847 (s, br) cm⁻¹) and in CH₃CN solution (1914 (m), 1865 (s) cm⁻¹). The absorption at 1830 cm⁻¹ in the infrared spectrum of the title compound is believed to be due to the interactions between the

Na⁺ cations and the oxygen atoms of the carbonyl groups in [Fe₂(CO)₈]²⁻.

The infrared spectrum of {[C₅H₅N]₄Na₂[Fe₂(CO)₈]}_∞ in THF also suggests the presence of ion pairing (three major absorptions are at 1922 (m), 1875 (s), and 1829 (m) cm⁻¹). However, the ¹³C NMR chemical shift of the title compound in THF-*d*₈, a singlet at δ 227.84 ppm for the carbonyls, fails to distinguish between unbound carbonyl groups and Na⁺-bound carbonyl groups at room temperature. The singlet remains at -80 °C. In CH₃CN and in pyridine, two major infrared absorptions at 1914 (m) and 1863 (s) cm⁻¹ are at the same positions as the absorptions from [PPh₄]₂[Fe₂(CO)₈], despite a noticeable shoulder at 1840 (w) cm⁻¹. These results indicate that the ion pairing in CH₃CN and in pyridine solutions is significantly reduced, if not totally absent. Other IR studies of Na₂[Fe₂(CO)₈] reveal three carbonyl bands at 1910 (m), 1860 (s) and 1835 (w) cm⁻¹ in DMF¹⁴ and at 1914 (sh), 1868 (s) and 1821 (m) cm⁻¹ in THF.¹⁵ These results suggest that contact ion pairing between Na⁺ and [Fe₂(CO)₈]²⁻ is also operative in DMF and THF.

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Supplementary Material Available: Listings of positional parameters, calculated hydrogen atom positional parameters, anisotropic thermal parameters, bond distances, and bond angles and a unit cell packing diagram (9 pages); a listing of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Syntheses and Molecular Structures of an Unusual Cyclic Tetrameric Organometallic Complex, {(CH₃)₂Al[μ-N(*i*-C₃H₇)₂]₂Mg(CH₃)₄}, Containing Tricoordinate Magnesiums, and a Linear Dimer, {(CH₃)₂Al[μ-N(C₂H₅)₂]₂Mg(CH₃)₂}, Containing Tetracoordinate Magnesiums

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Introduction

The reaction of trimethylaluminum with dialkylmagnesium is perhaps one of the most celebrated reactions in the aluminum magnesium mixed-metal chemistry. Investigations mostly concentrated on dialuminum magnesium complexes, e.g., Mg[Al(O-CH₃)₂(CH₃)₂]₂ and Mg[Al(CH₃)₄]₂.^{1,2} Monoaluminum magnesium complexes were synthesized in different laboratories;¹⁻⁶ however, the first example of an X-ray crystal structure of [Me₂Si(*i*-Bu)₂(AlMe₂)(MgI)]₂ was reported recently.⁵ Herein, we report the syntheses of {(CH₃)₂Al[μ-N(C₂H₅)₂]₂Mg(CH₃)₂}₂ (**1**) and {(CH₃)₂Al[μ-N(*i*-C₃H₇)₂]₂Mg(CH₃)₄}₂ (**2**) from the reactions of trimethylaluminum (Al(CH₃)₃) with bis(diethylamino)magnesium (Mg[N(C₂H₅)₂]₂) and bis(diisopropylamino)magnesium (Mg[N(*i*-C₃H₇)₂]₂), respectively.⁷ Surprisingly, four molecules of (CH₃)₂Al[μ-N(*i*-C₃H₇)₂]₂Mg(CH₃)₄ (**2a**) associate weakly as a tetramer (**2**) in the solid state through the interactions of tricoordinate magnesiums with carbons or/and

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