

(tetrahydrofuranacetato)cobalt(II), 4.9–5.1 BM, confirms the assignment of an octahedral geometry to this complex.<sup>7</sup> The moment of bis(tetrahydrofuroato)cobalt(II) is lower, however; moments of this magnitude have been observed for the octahedral complex hexakis-(pyridine N-oxide)cobalt(II) perchlorate, 4.69 BM,<sup>8</sup> potassium tris(acetylacetonato)cobalt(II), 4.79 BM,<sup>9</sup> and dinitratobis(triphenylphosphine oxide)cobalt(II), 4.69 BM.<sup>10</sup> The electronic absorption spectra of the two copper complexes are typical of copper(II) complexes and do not appear to have the "dimer" band at 375 nm identified by Yamada, *et al.*,<sup>11</sup> although a strong charge-transfer band centered at approximately 300 nm may be obscuring the relatively weak 375-nm band.

Bis(tetrahydrofuranacetato)copper(II) does not follow the Curie-Weiss law but rather shows a temperature-dependent magnetic moment. The temperature dependence is similar to the temperature dependence shown by the copper acetate dimer<sup>12</sup> and other copper-carboxylic acid complexes.<sup>13</sup> Thus a copper acetate dimer structure is suggested. Molecular weight measurements in chloroform confirm the dimeric nature of this compound (see Table II).

TABLE II

MOLECULAR WEIGHTS OF BIS(TETRAHYDROFUROATO)COBALT(II), BIS(TETRAHYDROFURANACETATO)COBALT(II), BIS(TETRAHYDROFUROATO)COPPER(II), AND BIS(TETRAHYDROFURANACETATO)COPPER(II) IN CHLOROFORM

Compound	Concn, g/100 g of solvent	Mol wt	Polymerizn no. <sup>a</sup>
Bis(tetrahydrofuroato)cobalt(II)	0.1548	1485	5.13
	0.2846	1443	4.95
	0.6433	1522	5.26
	1.6172	1773	6.12
Bis(tetrahydrofuranacetato)cobalt(II)	0.1816	1401	4.42
	0.4293	1635	5.15
	0.3550	1464	4.63
	1.4764	1400	4.42
Bis(tetrahydrofuroato)copper(II)	0.2939	1107	3.82
	1.1795	1398	4.81
Bis(tetrahydrofuranacetato)-copper(II)	0.2178	486	1.54

<sup>a</sup> The polymerization number is the experimental molecular weight divided by the molecular weight of the hypothetical monomeric complex.

Bis(tetrahydrofuroato)copper(II) follows the Curie-Weiss law with a normal magnetic moment. It is more highly associated in solution, and we believe it is best considered as a chelate involving ethereal oxygens. This is in agreement with the solution studies of Sigel, *et al.*,<sup>1</sup> on the 1:1 complex of this ligand with copper(II).

The differences observed between the two copper complexes are consistent with the different stabilities

expected for five- and six-member chelate ring formation.

The possibility that the cobalt complexes were polymers coordinated only by the carboxyl oxygens and different from simple carboxylic acid salts because of the steric effects of the ring was considered. Therefore, the sterically similar bis(phenylacetate)cobalt(II) and other carboxylate complexes were synthesized. These compounds in the anhydrous state were purple solids, insoluble in organic solvents and not at all similar to the ether complexes, but similar to other simple carboxylic acid derivatives of cobalt.

The metal complexes of TFA and TFAA have many properties consistent with ether coordination. They are water-sensitive and decompose in coordinating solvents, even such weakly coordinating solvents as acetone and alcohol. The infrared spectra show small shifts of the C–O–C band to lower frequencies for the tetrahydrofuroate complexes but not for the tetrahydrofuranacetate complexes. This type of shift has been recognized before<sup>3</sup> although it is not a definite test for ether coordination. The complexes did not show indications of water or free carboxylic acid in their infrared spectra.

Neither ether oxygens nor individual carboxyl oxygens are likely to serve as bridging donors in the manner commonly found for chloride ions. Therefore, in order to satisfy the observed stoichiometry and preserve six-coordination of the metal ions (as the above data require), it is necessary to bridge metal ions with the carboxyl group. This feature is of course familiar in the  $\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$  structure, but here it is combined with ether coordination. These complexes are quite different from those previously reported to be formed by the tetrahydrofurfurylamine ligand.<sup>14</sup> In view of these differences, it would appear risky to postulate ether coordination whenever halide is present for possible bridging. When the anion is perchlorate, or when the anion is part of the ligand itself, as in the present case, ether coordination can be firmly established.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FACULTY OF ENGINEERING SCIENCE, OSAKA UNIVERSITY, TOYONAKA, OSAKA, JAPAN

## Iron Carbonyl Complex of a Conjugated Azo Olefin

BY SEI OTSUKA, TOSHIKATSU YOSHIDA, AND AKIRA NAKAMURA

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Previously we have shown<sup>1</sup> that enimine systems ( $-\text{CH}=\text{CHCH}=\text{N}-$ ) can be coordinated to the  $\text{Fe}(\text{CO})_3$  moiety through the  $p\pi$ -conjugated double bonds like

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in butadiene iron carbonyl, whereas conjugated diimine ( $-\text{N}=\text{C}=\text{C}=\text{N}-$ ) forms a chelate coordination through the nitrogen lone pairs. An X-ray diffraction study on  $\text{Fe}(\text{CO})_3(\text{C}_6\text{H}_5\text{CH}=\text{CHCH}=\text{NC}_6\text{H}_5)$  confirmed the "so-called"  $\pi$ -coordination bonding.<sup>2</sup> It seems of interest from these works to examine the bonding scheme for coordination of an ene-azo system.

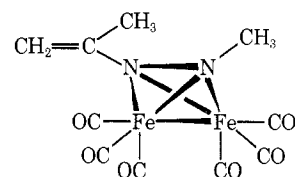
2-(Methylazo)propene  $\text{CH}_3\text{N}=\text{NC}(\text{CH}_3)=\text{CH}_2$  reacts readily with  $\text{Fe}_2(\text{CO})_9$  in benzene at ambient temperature affording orange-yellow, diamagnetic needles,  $\text{Fe}_2(\text{CO})_6(\text{C}_4\text{H}_8\text{N}_2)$ , mp 53–55°, in low yield. The mass spectrum shows fragment peaks of  $\text{Fe}_2(\text{CO})_{6-n}(\text{C}_4\text{H}_8\text{N}_2)^+$  ( $n = 1-6$ ) formed by successive loss of the six carbonyl groups. Such fragment ions as  $\text{N}_2\text{Fe}_2^+$ ,  $\text{Fe}_2^+$ , and  $\text{C}_4\text{H}_8\text{N}_2^+$  indicate the presence of an iron-iron bond and of an  $-\text{N}=\text{N}-$  bond. Evidence that the organic moiety in the complex is the methylazopropene retaining the original skeleton is ample in the fragments.

The nmr spectrum measured in  $\text{CCl}_4$  showed two slightly broad singlet resonances at  $\tau$  4.87 and 4.96 due to the vinylidene protons and two sharp singlet peaks at  $\tau$  6.79 and 8.05 assignable to the N-methyl and C-methyl protons, respectively. Corresponding chemical shifts of the free ligand in  $\text{CCl}_4$  are observed at  $\tau$  4.33, 4.37, 6.13, and 8.20, respectively. The insignificant upfield shift ( $\Delta\tau = 0.54$  and  $0.59$ ) of the vinylidene protons in the complex suggests that the C–C bond does not participate in coordination. Consistent with this is the chemical shift ( $\tau$  8.05) of the C-methyl protons, which should have been under diamagnetic shielding influence due to back-bonding from the iron(0) center if the double bond participates in the coordination. Various factors may be involved in governing the chemical shift of the N-methyl protons, e.g., (1) an upfield shift due to the change in hybridization of the nitrogen atom from  $\text{sp}^2$  to  $\text{sp}^3$ ,<sup>3</sup> (2) an anisotropic effect due to the metal atom field,<sup>4</sup> and (3) a deshielding effect due to lone-pair coordination of the nitrogen atom to the metal.<sup>2</sup> Although it is difficult to assess which factor is controlling, the observed upfield shift ( $\Delta\tau = 0.66$ ) renders the possibility of lone-pair coordination to the metal unlikely.

The ir spectrum measured in  $\text{CCl}_4$  showed six terminal carbonyl stretching frequencies ( $\text{cm}^{-1}$ ) at 2069 s, 2024 vs, 1991 vs, 1974 vs, 1913 s, and 1935 w. The band pattern resembles that of the binuclear complex  $\text{RNSFe}_2(\text{CO})_6$ ,<sup>5</sup> suggesting a similar disposition of the carbonyl groups with respect to the ligand axis ( $\text{N}-\text{N}$ ). The  $-\text{N}=\text{N}-$  stretching absorption ( $1500\text{ cm}^{-1}$ ) of the free ligand disappeared in the complex, but the absorptions at 1629 and  $891\text{ cm}^{-1}$ , assignable respectively to the  $\text{C}=\text{C}$  stretching and out-of-plane deformation of a vinylidene group, may be compared with those ( $1640\text{ cm}^{-1}$  for  $\nu_{\text{C}=\text{C}}$  and  $905\text{ cm}^{-1}$  for  $\delta(\text{CH})$ ) of the free ligand. Thus the ir data reinforce the conclusion from

the nmr spectrum that 2-(methylazo)propene participates in the coordination only through the azo group. The medium-intensity band at  $1107\text{ cm}^{-1}$  assignable to the N–N stretching is about  $390\text{ cm}^{-1}$  lower than that of the free azo ligand indicating considerable reduction in the bond order.

All of these physical characteristics can be accommodated in the proposed structure depicted below. We postulated that the two iron atoms attain the inert gas formalism as in many iron(0) complexes. The assumption requires that the two nitrogen atoms in  $\text{sp}^3$  hybridization state bridge two iron atoms through  $\sigma$ -type bonding. The same bonding scheme was postu-



lated for the closely related azobenzene complex,  $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{NNC}_6\text{H}_5)$ ,<sup>6</sup> or thionitroso complexes,  $\text{Fe}_2(\text{CO})_6(\text{RNS})$ .<sup>5</sup> The ene-azo complex is thermally fairly stable and air insensitive; decomposition is not appreciable in hydrocarbon solvents indefinitely when kept at ambient temperature. This contrasts with the aromatic congener  $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{NNC}_6\text{H}_5)$  which decomposes spontaneously in solution affording a "ureylene" complex,  $\text{Fe}_2(\text{CO})_6(\text{C}_6\text{H}_5\text{NCONC}_6\text{H}_5)$ .<sup>6</sup>

#### Experimental Section

A mixture of 2-(methylazo)propene, 0.186 g (2 mmol), and  $\text{Fe}_2(\text{CO})_9$ , 0.736 g (2 mmol), in 10 ml of benzene was stirred at ambient temperature for 45 hr, filtered, and evaporated under vacuum to give a reddish brown oil. The oil was chromatographed on  $\text{Al}_2\text{O}_3$  under nitrogen using a benzene-hexane mixture as an eluent to afford yellow eluate from which was obtained orange-yellow crystals. Recrystallization from hexane gave 25 mg of yellowish orange needles, mp 53–55°. *Anal.* Calcd for  $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_6\text{Fe}_2$ : C, 33.00; H, 2.21; N, 7.69; mol wt, 364. Found: C, 32.89; H, 1.72; N, 7.21; mol wt, 364.

The complex is readily soluble in polar and nonpolar solvents such as benzene, hexane, and  $\text{CHCl}_3$  and can be sublimed at  $80^\circ$  ( $10^{-3}$  mm). The ir spectrum recorded on a Jasco Model DS-402G grating spectrometer using Nujol mull showed bands ( $\text{cm}^{-1}$ ) at 2064 (vs), 2020 (vs), 1990 (vs), 1974 (vs), 1964 (vs), 1935 (w), 1629 (w), 1250 (m), 1172 (w), 1145 (sh), 1107 (m), 892 (m), 805 (w), 730 (m), and 670 (m). The nmr spectrum was measured by a 100-Mc Model JNM 4H-100 of Japan Electron Optics Laboratory in  $\text{CCl}_4$  using TMS as internal reference. Four singlets were observed at  $\tau$  4.87, 4.96, 6.97, and 8.05 with relative intensity of 1:1:3:3. The mass spectrum recorded on a Hitachi Type RMU-7HR showed the following  $m/e$  peaks: 364 (8),  $\text{C}_4\text{H}_8\text{N}_2\text{Fe}_2(\text{CO})_6^+$ ; 336 (80),  $\text{C}_4\text{H}_8\text{N}_2\text{Fe}_2(\text{CO})_5^+$ ; 308 (33),  $\text{C}_4\text{H}_8\text{N}_2\text{Fe}_2(\text{CO})_4^+$ ; 280 (30),  $\text{C}_4\text{H}_8\text{N}_2\text{Fe}_2(\text{CO})_3^+$ ; 252 (70),  $\text{C}_4\text{H}_8\text{N}_2\text{Fe}_2(\text{CO})_2^+$ ; 224 (100),  $\text{C}_4\text{H}_8\text{N}_2\text{Fe}_2(\text{CO})^+$ ; 196 (26),  $\text{C}_4\text{H}_8\text{N}_2\text{Fe}_2^+$ ; 169 (65); 153 (50); 140 (9),  $\text{N}_2\text{Fe}_2^+$ ; 139 (10); 138 (10),  $\text{NCFe}_2^+$ ; 126 (20),  $\text{NFe}_2^+$ ; 124 (9),  $\text{CFe}_2^+$ ; 112 (50),  $\text{Fe}_2^+$ ; 98 (13); 97 (13); 84 (18),  $\text{C}_4\text{H}_8\text{N}_2^+$ ; 56 (28),  $\text{Fe}^+$ . The figures in parentheses indicate the relative intensities.

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