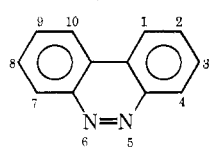
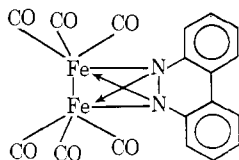


TABLE II
NMR SPECTRA

	Ligand		Complex	
	τ^a	H	τ	H
Benzo[c]cinnoline	1.42	4,7	2.15	1,10
	1.79	1,10		
	2.32	2,9,3,8		
3,8-Dichlorobenzo- [c]cinnoline	1.30	4,7	1.66	1,10
	1.58	1,10		
	2.16	2,9		
	2.83	4,7		
1,10-Dichlorobenzo- [c]cinnoline	1.44	4,7	2.5-3.0	Multiplet
	2.25	2,9,3,8		
Benzo[c]cinnoline 5-oxide	1.50	7	2.15	1,10
	1.99	1,10		
	2.40	2,9,3,8,4		

^a All of the peaks are multiplets.

On the basis of the above data we proposed¹ a structure analogous to Baikie and Mills' *o*-semidine structure and Dekker and Knox's azobenzene-type structure



wherein the Fe-Fe plane is perpendicular to the benzo-cinnoline plane and the N-N bond is not totally ruptured, but each N atom acts as a three-electron donor. The tetraazapyrene complex presumably has the Fe₂(CO)₆ structure complexed to each azo link. The infrared spectrum of **2** compared with the spectra of **1** and the N,N'-dioxide in the 1400-1620 cm⁻¹ region indicates a simplification in the complex compatible with lower N-N bond order.^{11,15}

Recent single-crystal X-ray analysis has now confirmed the proposed structure and has been reported on in detail in a separate communication.¹⁶ Preliminary data indicate the N-N bond to be a "normal" single bond of 1.40 Å. These values are similar to another recently reported¹⁷ complex which contains an N-N bond.

Experimental Section

Iron pentacarbonyl was purchased from GAF and used as received. The starting azo compounds were obtained commercially or prepared by literature procedures. In each case the complexes were characterized by elemental analysis and nmr (Varian A-60), ir (PE-221), and mass spectra (AEI MS-9). A general procedure, used for preparing all of the complexes, is given below. Column chromatography was the preferred purification procedure although some complexes could be sublimed.

Benzo[c]cinnolinehexacarbonyldiiron (2).—A mixture of benzo-[c]cinnoline (2.04 g, 0.0113 mol) and iron pentacarbonyl (4.43 g, 0.0226 mol) in decalin (50 ml) was heated with stirring at 150° until gas evolution ceased (about 1 hr). The mixture was cooled and filtered and the red filtrate chromatographed on alumina. Petroleum ether (bp 30-60°) was used to elute the decalin. Petroleum ether-benzene (4:1) eluted the complex, dark red

(15) We gratefully acknowledge the assistance of Mr. Norman Colthup in interpreting the infrared spectra.

(16) R. J. Doedens, *Inorg. Chem.*, **9**, 429 (1970).

(17) R. J. Doedens and J. A. Ibers, *ibid.*, **8**, 2709 (1969).

crystals, 4.1 g (79%), mp 145° dec. *Anal.* Calcd for C₁₅H₈N₂O₆Fe₂: C, 46.99; H, 1.75; N, 6.09; O, 20.87; Fe, 24.28. Found: C, 47.38; H, 1.79; N, 6.24; O, 20.73; Fe, 24.18.

3,8-Dichlorobenzo[c]cinnolinetriphenylphosphinepentacarbonyldiiron.—3,8-Dichlorobenzo[c]cinnolinehexacarbonyldiiron (0.21 g, 0.0004 mol) and triphenylphosphine (0.10 g, 0.0004 mol) in benzene (35 ml) were heated at reflux for 2 hr. The solution was cooled and the solvent was evaporated under vacuum. The red solid product was triturated with petroleum ether and ethanol resulting in an orange solid, 0.2 g (66%), mp 215° dec. *Anal.* Calcd for C₃₅H₂₁N₂O₅Cl₂PF₂: C, 55.08; H, 2.77; N, 3.67; Cl, 9.29; P, 4.06; Fe, 14.64. Found: C, 55.11; H, 2.80; N, 4.08; Cl, 9.32; P, 4.36; Fe, 14.92.

CONTRIBUTION NO. 1636 FROM THE
CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND COMPANY,
WILMINGTON, DELAWARE 19898

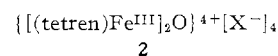
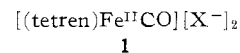
Complexes of Tetraethylenepentamine with Iron(II) and Iron(III). An Iron(II) Carbonyl Derivative

BY L. RUSSELL MELBY

Received January 8, 1970

Tetraethylenepentamine (tetren) forms well-characterized complexes with Co(II), Co(III), Cr(III),¹⁻⁴ and Cu(II).⁵ Stability constants with other transition metal ions⁶⁻⁸ and several nontransition metal ions⁸ have been determined, but published work with iron has been limited to a stability constant measurement and unsuccessful attempts to prepare complexes with Fe(II) and Fe(III)⁶ and an examination of the Fe(III) derivative, in solution, as a catalyst for hydrogen peroxide decomposition.⁹

This note describes the isolation of crystalline complexes of tetraethylenepentamine with Fe(II) wherein carbon monoxide occupies the sixth coordination position (**1**) and of acidotetraethylenepentamine complexes of Fe(III) wherein the two iron atoms are presumably oxygen bridged to form the dimeric species **2**.¹⁰



Experimental Section

Tetraethylenepentamine was vacuum distilled and the fraction of bp 155-160° (1.0-1.5 mm) was used. Hydriodic acid

(1) H. B. Jonassen and F. W. Frey, *J. Amer. Chem. Soc.*, **75**, 1524 (1953).

(2) J. Selbin, *J. Inorg. Nucl. Chem.*, **17**, 84 (1961).

(3) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966).

(4) D. A. House and C. S. Garner, *ibid.*, **6**, 272 (1967).

(5) G. G. Schlessinger, *Gannon Coll. Chem. J.*, **1** (1965); *Chem. Abstr.*, **64**, 189336 (1966).

(6) H. B. Jonassen, A. Schaafsma, and L. Westerman, *J. Phys. Chem.*, **62**, 1022 (1958).

(7) D. W. Margerum and J. D. Carr, *J. Amer. Chem. Soc.*, **88**, 1639 (1966).

(8) C. N. Reiley and A. Vavoulis, *Anal. Chem.*, **31**, 243 (1959).

(9) G. Wada, T. Nakamura, K. Terauchi, and T. Naka, *Bull. Chem. Soc. Jap.*, **37**, 447 (1964); *Chem. Abstr.*, **61**, 9157e (1964).

(10) I wish to thank a referee for suggesting this possibility. I had originally proposed a monomeric structure with an iron-amide bond formed by abstraction of a proton from an amino group of the ligand.

(55%) was freshly distilled from hypophosphorous acid. All other chemicals were reagent grade.

Solution infrared spectra were taken in Irtran-2 cells¹¹ (0.025 mm) on a Perkin-Elmer Model 237 and mull spectra were taken on a Perkin-Elmer Model 621 spectrophotometer.

(tetren)Fe^{II}CO²⁺ in Water.—To a solution of 2.8 g (15 mmol, 75 mequiv) of tetraethylenepentamine in 5 ml of deaerated water, under nitrogen with cooling and stirring, was slowly added 6 ml of concentrated hydrochloric acid, and then 1.4 g (5 mmol) of ferrous sulfate heptahydrate was added. The mixture was stirred until the ferrous sulfate had dissolved, filtered under nitrogen, and alkalinized to pH 8.5 with 6 *N* sodium hydroxide. Carbon monoxide was passed into the solution which rapidly changed from light green to deep dichroic red-green. After 3 hr a portion was transferred, with exclusion of air, to an Irtran-2 infrared cell; the spectrum showed a strong, sharp coordinated CO band at 1940 cm⁻¹. The CO band was eliminated by passing nitrogen or argon through the solution for 16 hr but was restored by passing carbon monoxide in for 3 hr.

[(tetren)Fe^{II}CO][Cl][ClO₄] (3).—A solution was prepared as above, carbon monoxide was passed in for 16 hr, and 5 g of sodium perchlorate in 5 ml of deaerated water was added. The flask was packed in ice and kept cold for 2 hr while carbon monoxide addition was continued. The yellow-brown crystalline rosette clusters were collected on a filter in the absence of air and washed by decantation with ethanol. Exposure to air was now permissible and the solid was washed on the filter with ethanol and then with ether. The material was briefly air dried and then vacuum dried for 2 hr. It is reasonably stable at room temperature but is best stored in a freezer. The yield was 1.4 g (68%). *Anal.* Calcd for C₉H₂₃Cl₂FeN₅O₈ (formula weight 408): C, 26.5; H, 5.7; Cl, 17.4; Fe, 13.7; N, 17.2. Found: C, 26.3; H, 5.8; Cl, 17.1; Fe, 13.8; N, 16.9.

[(tetren)Fe^{II}CO][ClO₄]₂ (4).—To a solution of 2.8 g of tetraethylenepentamine in 5 ml of water, under nitrogen, was added dropwise, with cooling and stirring, 6 ml of 72% perchloric acid. To this solution was added 1.4 g of ferrous sulfate heptahydrate and 4 ml of water, and stirring was continued until the salt had dissolved. The solution was filtered in the absence of air, carbon monoxide was continuously passed in, and 6 *N* sodium hydroxide added to achieve pH 8.5. Carbon monoxide was passed through for 5 hr, a solution of 5 g of sodium perchlorate in 5 ml of water was added, the gas inlet tube was removed and the flask was stoppered and stored overnight in a refrigerator. The dull tan needles were collected and washed as above; yield, 0.2 g (8%). *Anal.* Calcd for C₉H₂₃Cl₂FeN₅O₉ (formula weight 472): C, 23.0; H, 4.9; N, 14.8. Found: C, 22.8; H, 4.9; N, 14.7.

[(tetren)Fe^{II}CO][I]₂ (5).—A solution prepared from 5.6 g of tetraethylenepentamine, 10 ml of water, 21 ml of 55% hydriodic acid, and 2.8 g of ferrous sulfate, under a carbon monoxide atmosphere, was alkalinized to pH 8.5 with 6 *N* sodium hydroxide and was transferred to a pressure bottle flushed with carbon monoxide. The bottle was pressured to 3 atm with carbon monoxide and allowed to stand undisturbed at room temperature for 3 days. A brown stalagmitic crystalline deposit had formed. After pressure release the supernatant liquid was quickly decanted (nitrogen or carbon monoxide atmosphere), and the product was washed by decantation with ethanol, then collected and washed on a funnel with ethanol and ether, and vacuum dried; yield, 3.0 g (57%). When the mixture was allowed to stand for 6 days, the yield was 76%. *Anal.* Calcd for C₉H₂₃FeI₂N₅O (formula weight 527): C, 20.5; H, 4.4; Fe, 10.6; I, 48.1; N, 13.3. Found: C, 20.6; H, 4.3; Fe, 10.3; I, 47.9; N, 13.4.

{[(tetren)Fe^{III}]₂O}[I]₄ (6).—To a solution of 5.7 g of tetraethylenepentamine in 25 ml of deaerated water was added 25 ml of 6 *N* hydrochloric acid, and to this was added, under nitrogen, a filtered solution of 2.8 g of ferrous sulfate in 10 ml of deaerated water. Still under nitrogen, the solution was alkalinized to pH 8.5 with 6 *N* NaOH, and a solution of 5.0 g of potassium iodide in 10 ml of water was added. The solution was poured into a large

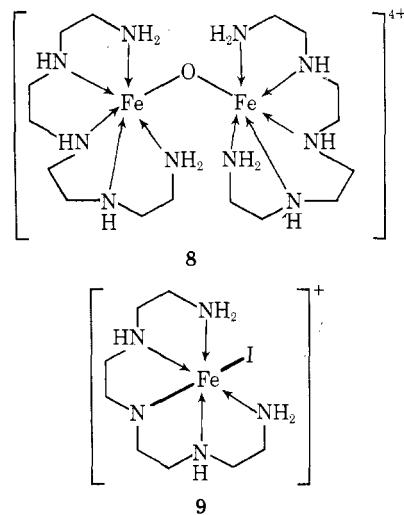
crystallizing dish and allowed to stand in air for 2 hr. The shiny brownish black crystals were collected on a coarse-frit funnel, washed very quickly with one 20-ml portion of ice-cold water, and then washed by decantation with several portions of ethanol. Finally, the product was washed on the funnel in the usual way with ethanol and ether and vacuum dried; yield, 1.8 g (34%). *Anal.* Calcd for C₁₈H₄₆Fe₂I₄N₁₀O (formula weight 1014): C, 19.0; H, 4.5; Fe, 11.0; N, 13.8. Found: C, 19.5; H, 4.7; Fe, 11.2; N, 13.9.

{[(tetren)Fe^{III}]₂O}[Cl₂][ClO₄]₂·3H₂O (7).—A half-scale preparation as described for 5 was carried out, but instead of potassium iodide a mixture of 5 g of solid sodium chloride and 3 g of sodium perchlorate was stirred into the solution in an erlenmeyer flask under nitrogen. The flask was then allowed to stand open to the air for 16 hr; black crystals in a dark purple supernatant fluid had formed. The crystals were collected as described above; yield, 0.5 g. *Anal.* Calcd for C₁₈H₅₂Cl₄Fe₂N₁₀O₂ (formula weight 830): C, 23.2; H, 6.3; Cl, 17.1; Fe, 13.5; N, 16.8. Found: C, 23.2; H, 5.8; Cl, 16.7; Fe, 13.0; N, 16.3.

Discussion

The assigned formulations of the CO complexes 3–5 are evident from their elemental compositions and infrared spectra but acquisition of other structural information is complicated by their insolubility in all but aqueous media and by their instability in solution. They dissolve in water with gas evolution, and even with rigorous exclusion of air rustlike decomposition products are formed.

As to the Fe(III) complexes, elemental analysis would not distinguish between the oxygen-bridged dimeric structure 8 and an amide-iron bonded monomeric structure such as 9. However, the room-temper-



ature magnetic susceptibility of the iodide 6 corresponds to 1.95 BM per iron atom which decreased to 1.2 BM at 196°K.¹² This temperature dependence argues against an isolated Fe(III) ion as in 9 but can be accounted for by assuming weak antiferromagnetic coupling between unpaired electrons of two low-spin Fe(III) ions mediated by an oxide bridge as in 8.

Commercially available tetraethylenepentamine is usually a mixture of isomers and higher and lower homologs, and simple fractional distillation serves at best to concentrate pentamine isomers. It seems certain that

(11) Barnes Engineering Co., Stamford, Conn.

(12) I am indebted to Dr. J. F. Weiher of this laboratory for the magnetic susceptibility measurements.

these complexes incorporate only the linear pentamine since identical results were obtained with pentamine purified *via* the hydrochloride⁸ as with distilled pentamine fraction. Moreover, amine isolated by acidic decomposition of the complexes was shown by gas chromatography to comprise only one component and its retention time was identical with that of the major peak from hydrochloride-purified amine.

In their work on complexes of the type [(tetren)CoCl]₂[X⁻]₂, House and Garner were able to distinguish between geometrical isomers, mainly on the basis of differences in NH₂ bending and NH stretching frequencies.³ The major infrared bands for the iron complexes are listed in Table I, but these data cannot be correlated

TABLE I
INFRARED SPECTRA OF
TETRAETHYLENEPENTAMINE-IRON DERIVATIVES^a

Compd	Assignment and freq, cm ⁻¹		
	NH ₂ str	CO	NH ₂ bend
3	3310 m	1940 vs	1620 m
	3140 s		1600 w
4	3270 s	1960 vs	1600 m
5	3150 s	1950 vs	1600 m
6	3150 vs ^b		1580 s
7	3200 s ^{b,c}		1650 w
			1590 m

^a Nujol mulls. ^b Doublet. ^c Also 3450 cm⁻¹ assigned to H₂O.

with those of House and Garner so the question of geometry remains open.

Acknowledgments.—The author wishes to thank Dr. G. W. Parshall for helpful discussions and Miss Eleanor G. Applegate for technical assistance.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTHERN CALIFORNIA,
LOS ANGELES, CALIFORNIA 90007

The Action of Dimethyl Sulfide on Pentaborane(9)¹

BY INDU B. MISHRA AND ANTON B. BURG

Received February 16, 1970

New insight into the action of bases on pentaborane(9) comes from its vapor-phase reaction with dimethyl sulfide at temperatures above 75°, to form diborane (or a BH₃ complex) and a resin containing (CH₃)₂S. Stronger aprotic bases such as trimethylamine were known to form 2:1 solid adducts with B₅H₉,²⁻⁴ but heating these with excess base (in a closed chamber) produced 2 units of the base-BH₃ complex per B₅H₉. It

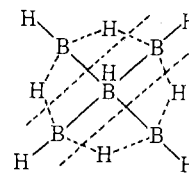
(1) It is a pleasure to acknowledge the generous support of this research by the Office of Naval Research.

(2) A. B. Burg, *J. Amer. Chem. Soc.*, **79**, 2129 (1957).

(3) A. B. Burg, XVIIth International Congress of Pure and Applied Chemistry, Butterworths, London, 1960, p 57.

(4) M. L. Denniston and S. G. Shore, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. INOR 104.

seemed obvious that the base directly removed BH₃ from the structural pattern

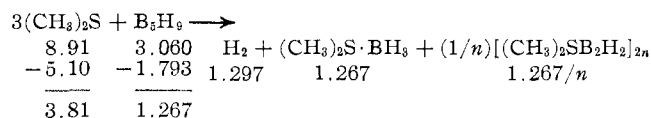


leaving (BH)₃ to form the observed thermally stable resin containing the base.² The same process seemed evident in the B₅H₉-induced trimerization of (CH₃)₂NBH₂, wherein (CH₃)₂NBH₂·B₄H₈ could be recognized as an intermediate.⁵ However, no base as weak as (CH₃)₂S could attack B₅H₉ by first removing BH₃, for the complex (CH₃)₂S·BH₃ is extensively dissociated in the vapor phase,⁶ as B₅H₉ itself is not. Instead, then, it appears that (CH₃)₂S invades B₅H₉ to displace BH₃ and attach itself to the remaining B₄H₈ moiety, which then undergoes a condensation to resin. The driving force of the reaction would be the extreme Lewis-acid strength of the B₄H₈ moiety, beginning to take effect as the B-H-B bridges in B₅H₉ are loosened by thermal vibration. Thus it now seems reasonable that stronger bases, which require similar temperatures for dismemberment of B₅H₉, also first seize B₄H₈ and displace BH₃, although the order of events is less obvious because the displaced BH₃ is irreversibly captured by these strong bases.

Experimental Section

In the initial experiment, a mixture of B₅H₉ with excess (CH₃)₂S was heated at 75-90°, forming hydrogen, nonvolatile solids, and diborane, which appeared as the dissociable complex (CH₃)₂S·BH₃ on condensation at 25°.⁶ However, the decomposition of some of the diborane prevented a quantitative interpretation.

For a better experiment, we employed a vertical double-walled reaction vessel, with a 5 × 18 cm outer tube electrically heated to temperatures as high as 250°, while the inner 2.5 × 12 cm cold-finger was cooled to -33° by refluxing liquid ammonia. A lower tubulature at -23° collected BH₃ as the (CH₃)₂S complex while the B₅H₉-(CH₃)₂S mixture refluxed from the -33° cold-finger. Under these conditions it was possible to prove a quantitative process by the millimole stoichiometry accompanying the equation



This process was conducted in a series of stages at higher and higher outer wall temperatures. During 48 hr at 100° the progress was only 2%; in 9 hr at 135°, 6%; in 9 hr at 185°, 17%; and in 3 hr at 250-260°, 25%. The effective reaction temperatures must have been much lower, on account of rapid convection between the inner and outer walls.

The nonvolatile solid product included an amorphous resin but also a more definitely crystalline component, the X-ray powder pattern of which appeared as a series of peaks above a broad continuum. The relative displacements were 3.18 (s), 3.99 (m), 4.31 (w), 4.58 (w), 5.16 (w), and 5.75 (vw).⁷ Also

(5) A. B. Burg and J. S. Sandhu, *J. Amer. Chem. Soc.*, **89**, 1626 (1967).

(6) A. B. Burg and R. I. Wagner, *ibid.*, **76**, 3307 (1954).

(7) Kindly recorded for us by Dr. D. F. Palmer of our Department of Geological Sciences.