

etry and the bond lengths of these groups are in the correct ranges, except those of the disordered monodentate carboxylate: in particular, the C(72)—F distances, which are very inaccurate, range from 1.09 to 1.44 Å [mean value = 1.315 (3) Å] whereas the other C—F distances are dispersed within the standard deviations [mean value 1.276 (8) Å].*

The two cryptand molecules, related by an inversion center, have an *endo-endo* conformation. The distances and angles have correct values. One of the three chains appears disordered in one carbon position only. The crystal packing is shown in Fig. 2; no significant contact is observed between the tetramer and cryptand units since all the C...F contacts are greater than 3.14 Å.

* See deposition footnote.

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Structures of $[(C_2H_5)_4N]_2[In_2Fe_6(CO)_{24}]$ and $[(C_2H_5)_4N][(2,2'-bipyridine)InFe_2(CO)_8]$

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Abstract. Bis(tetraethylammonium) bis[[di- μ -carbonyl-bis[tricarbonylferrio(*Fe-Fe*)]- μ -(tetracarbonylferrio)-indiumate(1⁻)], $2C_8H_{20}N^+ \cdot [Fe_6In_2(CO)_{24}]^{2-}$, $M_r = 1497.48$, orthorhombic, *Cmca*, $a = 18.928$ (2), $b = 17.051$ (8), $c = 17.245$ (4) Å, $V = 5566$ (4) Å³, $Z = 4$, $D_x = 1.79$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 23.95$ cm⁻¹, $F(000) = 2960$, $T = 296$ K, $R = 0.042$, $wR = 0.054$ for 1794 unique reflections with $I > 3\sigma(I)$. $[(C_2H_5)_4N]_2[In_2Fe_6(CO)_{24}]$ consists of a central In_2Fe_2 parallelogram with each In atom linked to an additional $[Fe_2(CO)_6(\mu-CO)_2]$ group in a distorted tetrahedral array. The In_2Fe_2 parallelogram sits on a crystallographic site of $2/m$ symmetry. Tetraethylammonium (2,2'-bipyridyl)bis-(tetracarbonylferrio)indiumate(1⁻), $C_8H_{20}N^+ \cdot [Fe_2In(CO)_8(C_{10}H_8N_2)]^-$, $M_r = 737.04$, triclinic, *P1*, $a = 10.060$ (4), $b = 11.567$ (7), $c = 14.024$ (6) Å, $\alpha = 93.79$ (9), $\beta = 95.04$ (3), $\gamma = 107.65$ (6)°, $V = 1542$ (3) Å³, $Z = 2$, $D_x = 1.59$ g cm⁻³, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 17.06$ cm⁻¹, $F(000) = 740$, $T = 296$ K, $R = 0.063$, $wR = 0.087$ for 4853 unique observed reflections with $I > 3\sigma(I)$. $[(C_2H_5)_4N] \cdot [(bpy)InFe_2(CO)_8]$ (*bpy* = 2,2'-bipyridine) crystallizes with the $Fe(CO)_4$ groups and the bipyridine ligand in

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- CHARPIN, P., LANCE, M., NIERLICH, M., VIGNER, D., LIVET, J. & MUSIKAS, C. (1986). *Acta Cryst.* **C42**, 1691–1694.
 COTTON, A. F., MARLER, D. O. & SCHWOTZER, W. (1984). *Inorg. Chim. Acta*, **95**, 207–209.
 FRENZ, B. A. (1985). *Enraf-Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf-Nonius, Delft, The Netherlands.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 LINTVEDT, R. L., HEEG, M. J., AHMAD, M. J. & GLICK, M. D. (1982). *Inorg. Chem.* **21**, 2350–2356.
 PERRIN, A. (1977). *J. Inorg. Nucl. Chem.* **39**, 1169–1172.
 VILLARDI, G. C. DE, CHARPIN, P., COSTES, R. M., FOLCHER, G., PLURIEN, P., RIGNY, P. & DE RANGO, C. (1978). *J. Chem. Soc. Chem. Commun.* pp. 90–92.
 WALKER, N. & STUART, D. (1983). *Acta Cryst.* **A39**, 158–166.

a distorted tetrahedral arrangement around the In atom. The $[Fe(CO)_4]$ groups exhibit trigonal bipyramidal geometries.

Introduction. A number of different iron-carbonyl-containing indium compounds have been synthesized, including $[(C_2H_5)_4N][Fe(CO)_2CpInPh_3]$ (Burlitch, Leonowicz, Petersen & Hughes, 1979), $\{[(C_6H_5)_3P]_2N\}_2[Fe(CO)_4InBr_3]$, $\{[(C_6H_5)_3P]_2N\} \cdot [Fe(CO)_4InBr_2]$, $\{[(C_6H_5)_3P]_2N\} \cdot [Fe(CO)_4InBr_2(L)]$ [$L = N(C_2H_5)_3$, pyridine] (Ruff, 1968), $\{[Fe(CO)_2Cp]_2InX(L)\}$ ($X = Br, Cl$; $L = THF, p$ -dioxan), $[Fe(CO)_2CpInBr_2(L)]$ ($L = THF, p$ -dioxan) (Hsieh & Mays, 1971) and $[Fe_2(CO)_8\{\mu-InMn(CO)_5\}_2]$ (Preut & Haupt, 1979). Recently several novel Tl-Fe carbonyl compounds have been synthesized and structurally characterized. These compounds include $[(C_2H_5)_4N]_2[Tl_2Fe_4(CO)_{16}]$ (Whitmire, Cassidy, Rheingold & Ryan, 1987), and its Lewis base adducts (Cassidy & Whitmire, 1989), $[(C_2H_5)_4N]_4 \cdot [Tl_4Fe_8(CO)_{30}]$, $[(C_2H_5)_4N]_6 \cdot [Tl_6Fe_{10}(CO)_{36}]$ (Whitmire, Cassidy, Rheingold & Ryan, 1987), and $\{[(C_6H_5)_3P]_2N\}_2[Tl_2Fe_6(CO)_{24}]$ (Cassidy & Whitmire, 1989). Consequently we decided to try to synthesize some In-Fe carbonyl complexes by methods similar to those developed for thallium. The structures of

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two such compounds, [(C₂H₅)₄N]₂[In₂Fe₆(CO)₂₄] and [(C₂H₅)₄N][(bpy)InFe₂(CO)₈], are described herein.

Experimental. [(C₂H₅)₄N]₂[In₂Fe₆(CO)₂₄] was synthesized by two different methods. The first preparation involved addition of InCl₃ to a stirred Fe(CO)₅/KOH/CH₃OH solution in a 1:1 In:Fe ratio. [(C₂H₅)₄N]₂[In₂Fe₆(CO)₂₄] also resulted from the reaction of InCl₃ with [(C₂H₅)₄N]₂[Fe₂(CO)₈] in CH₃OH. An infrared spectrum in CH₃CN showed absorptions at 2036 (*m*), 2006 (*vs*), 1952 (*s*), 1928 (*m*), 1870 (*vw*), 1798 (*w*) and 1780 (*w*) cm⁻¹. A red rectangular crystal, 0.2 × 0.1 × 0.2 mm, of [(C₂H₅)₄N]₂[In₂Fe₆(CO)₂₄] was grown from a concentrated CH₃CN solution, and was mounted on the tip of a glass fiber with epoxy cement. Crystal data were collected (2θ-ω scans) with a Rigaku AFC5S four-circle diffractometer [Rigaku CONTROL(4:1:0) Automatic Data Collection Series (Molecular Structure Corporation, 1988a)]. The unit-cell constants were determined from the least-squares fit of 25 random reflections (6.71 ≤ 2θ ≤ 14.99°), which indicated a C-centered orthorhombic cell. Laue symmetry was checked and confirmed the orthorhombic Laue group *mmm*. Three standard reflections, $\bar{1}13$, $\bar{1}\bar{1}3$ and $\bar{2}21$, selected to give a good distribution in χ, were measured after every 150 reflections and showed an average loss in intensity of 2.8% by completion of data collection. Excluding standards, 3519 reflections were measured for the octant +*h*, +*k*, +*l*, *h*: 0 to 22, *k*: 0 to 25, *l*: 0 to 22, with 2θ_{max} = 55° and [(sinθ)/λ]_{max} = 0.65 Å⁻¹. Laue symmetry and systematic absences indicated the space group *Cmca* (No. 64). The data were collected in a non-standard cell setting, and were transformed to the standard setting of +*h*, +*k*, -*l*. No equivalent reflections were measured and 1794 were observed [*I* > 3σ(*I*)]. The structure was solved using the program MITHRIL (Gilmore, 1983) to locate the heavy atoms, followed by least-squares refinement and Fourier syntheses using the TEXSAN structure analysis package (Molecular Structure Corporation, 1988b) to locate the remaining non-H atoms. The cation H atoms were not located or refined. Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o)]^{-1}$ with all atoms refined anisotropically. The data were corrected for absorption (ψ scans, transmission range 0.8247–1.0000) and for Lorentz-polarization effects, but not for decay. Final least-squares refinement converged with *R* = 0.042, *wR* = 0.054, number of variables = 182, (Δρ)_{max} = 0.50 e Å⁻³, (Δ/σ)_{max} = 0.07 and *S* = 1.26.

[(C₂H₅)₄N][(bpy)InFe₂(CO)₈] was synthesized from a starting compound believed to be [(C₂H₅)₄N]₂[In₂Fe₄(CO)₁₆] (see below), which is synthesized from the addition of InCl₃ to a methanolic Fe(CO)₅/KOH solution in an approximate 1:2 In:Fe ratio.

Addition of 2,2'-bipyridine to this orange compound in CH₃OH resulted in an orange-red precipitate. The solid was redissolved in CH₃CN, filtered and CH₃OH was layered on top. Concentration under a stream of N₂ gas gave red-orange prismatic crystals which were suitable for X-ray analysis. After about two weeks of cooling, dark red needle-like crystals also formed. These crystals were of poor quality and attempts at structure determination were unsuccessful. The IR spectrum of the orange crystals (cm⁻¹, CH₃CN vs polystyrene) was composed of three carbonyl bands: 1987 (*m*), 1961 (*s*), 1875 (*vs*, *br*). The ¹H NMR spectrum was consistent with structural data: (p.p.m., CD₃CN) Et₄N⁺, 1.20 (*t*), 3.15 (*q*); [(bpy)-InFe₂(CO)₈]⁻, 7.68 (*t*), 8.17 (*t*), 8.45 (*d*), 8.85 (*d*). An orange rectangular prism, 0.3 × 0.2 × 0.4 mm, was mounted on the tip of a glass fiber with epoxy cement. The crystal lattice was determined from the least-squares fit of 25 reflections (7.45 ≤ 2θ ≤ 13.73°). Data were collected for *h*: 0–15, *k*: -18–18, *l*: -13–13, with 2θ_{max} = 55° and [(sinθ)/λ]_{max} = 0.65 Å⁻¹. Of the 7411 measured reflections, 7057 were independent (*R*_{int} = 1.2%) and 4853 were observed [*I* > 3σ(*I*)]. The three standard reflections (112, $\bar{1}\bar{1}\bar{1}$, 102), measured every 150 reflections, showed significant decay during data collection, with a final average intensity loss of 40.7%. The structure was solved by the direct-methods program SHELXS86 (Sheldrick, 1986) to locate the heavy atoms, followed by least-squares refinement and Fourier syntheses, from the TEXSAN structure analysis package, to locate the remaining non-H atoms. Full-matrix least-squares refinement minimized $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o)]^{-1}$ with the In and Fe atoms refined anisotropically. The H atoms on the bipyridine ligand were located at calculated positions. The tetraethylammonium cations were disordered at the α carbons. This disorder was resolved into two sets of positions whose populations refined to a 2:1 ratio. These populations were then fixed for subsequent refinement cycles. The H atoms on the [(C₂H₅)₄N]⁺ cations were not included in the refinement. The data were corrected for decay, for absorption (ψ scans, transmission range 0.8286–1.0000) and for Lorentz-polarization factors. Final least-squares refinement converged with *R* = 0.063, *wR* = 0.087, number of variables = 192, (Δρ)_{max} = 0.95 e Å⁻³, (Δ/σ)_{max} = 0.01 and *S* = 2.31.

Scattering factors from *International Tables for X-ray Crystallography* (Cromer & Waber, 1974).

Discussion. The asymmetric unit of the first compound consists of ½ of a tetraethylammonium cation and ¼ of the [In₂Fe₆(CO)₂₄]²⁻ anion. The [(C₂H₅)₄N]⁺ group lies on a twofold axis, while [In₂Fe₆(CO)₂₄]²⁻ is situated about a center of 2/*m* symmetry. Thus, two ordered [(C₂H₅)₄N]⁺ cations

and one ordered $[\text{In}_2\text{Fe}_6(\text{CO})_{24}]^{2-}$ anion form the complete molecule. It is isoelectronic and isostructural with the recently reported $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}_2[\text{Ti}_2\text{Fe}_6(\text{CO})_{24}]$ (Cassidy & Whitmire, 1989). The anion, $[\text{In}_2\text{Fe}_6(\text{CO})_{24}]^{2-}$, consists of a central In_2Fe_2 parallelogram with each In atom linked to an additional $\text{Fe}_2(\text{CO})_6(\mu\text{-CO})_2$ group. The $\text{In}\cdots\text{In}$ and $\text{Fe}\cdots\text{Fe}$ distances across the ring are long and considered nonbonding. For comparison, the $\text{In}\cdots\text{In}$ and $\text{Fe}\cdots\text{Fe}$ distances in $[\text{Fe}_2(\text{CO})_8\{\mu\text{-InMn}(\text{CO})_5\}]_2$ are 3.250 (1) and 4.218 (1) Å, respectively (Preut & Haupt, 1979), and the $\text{In}\text{---}\text{In}$ length in $\text{In}_2\text{Br}_3\cdot\text{I}\cdot\text{TMEDA}$ (TMEDA = *N,N,N',N'*-tetramethylenediamine) is 2.775 (2) Å (Khan, Peppe & Tuck, 1984). The In atoms in $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{In}_2\text{Fe}_6(\text{CO})_{24}]$ each exhibit a distorted tetrahedral coordination, whereas the ring Fe atoms are coordinated in a *cis* pseudo-octahedral fashion. An ORTEP (Johnson, 1976) diagram of the anion is shown in Fig. 1 and a stereoview is given in Fig. 2. The positional parameters for $[\text{In}_2\text{Fe}_6(\text{CO})_{24}]^{2-}$ are located in Table 1, and selected intramolecular distances and angles are found in Table 2.*

* Lists of structure factors, anisotropic thermal parameters, all coordinates, bond lengths, bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52897 (86 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

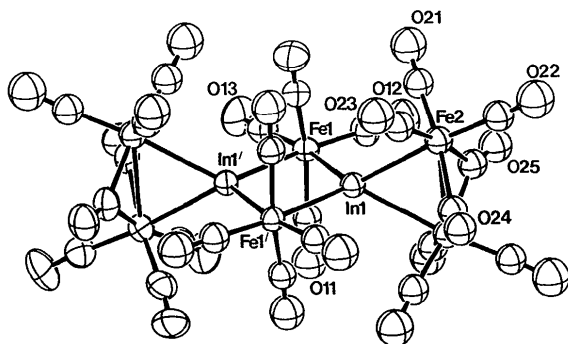


Fig. 1. ORTEP (Johnson, 1976) diagram of $[\text{In}_2\text{Fe}_6(\text{CO})_{24}]^{2-}$ with each C atom labeled according to the O atom to which it is bonded.

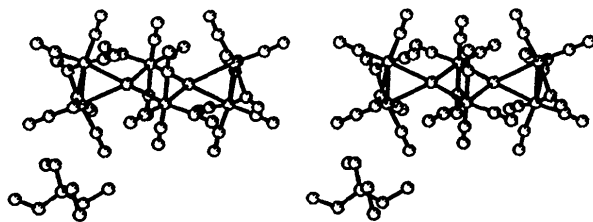


Fig. 2. Stereoview of $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{In}_2\text{Fe}_6(\text{CO})_{24}]$ showing the complete anion and the unique cation per molecule.

Table 1. Positional parameters and B_{eq} values for $[\text{In}_2\text{Fe}_6(\text{CO})_{24}]^{2-}$

$$B_{eq} = 8\pi^2/3(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
In1	1	0.06804 (4)	0.57083 (4)	3.21 (3)
Fe1	1	-0.08992 (8)	0.58414 (8)	3.22 (6)
Fe2	1.06911 (6)	0.16340 (6)	0.67092 (6)	4.08 (5)
O11	0.8481 (3)	-0.0650 (4)	0.5627 (4)	6.4 (3)
O12	1	-0.0834	0.7531 (5)	7.1 (5)
O13	1	-0.2604 (5)	0.5699 (5)	6.9 (5)
O21	1.1571 (4)	0.0290 (4)	0.7113 (4)	7.2 (4)
O22	1.1324 (4)	0.2729 (4)	0.7823 (5)	7.8 (4)
O23	1.1571 (3)	0.2104 (4)	0.5391 (4)	6.8 (4)
O24	1	0.3051 (5)	0.6080 (5)	5.9 (5)
O25	1	0.0970 (5)	0.8114 (5)	5.6 (4)
C11	0.9080 (4)	-0.0727 (4)	0.5703 (4)	4.2 (3)
C12	1	-0.0828 (6)	0.6877 (7)	4.3 (5)
C13	1	-0.1933 (7)	0.5756 (7)	4.8 (6)
C21	1.1211 (5)	0.0796 (5)	0.6936 (5)	5.0 (4)
C22	1.1062 (4)	0.2311 (5)	0.7389 (5)	5.1 (4)
C23	1.1208 (5)	0.1902 (5)	0.5873 (5)	4.8 (4)
C24	1	0.2425 (7)	0.6369 (6)	4.6 (6)
C25	1	0.1258 (7)	0.7506 (7)	4.6 (5)

Table 2. Selected bond distances (Å) and angles (°) for $[\text{In}_2\text{Fe}_6(\text{CO})_{24}]^{2-}$

In1—Fe1	2.698 (2)	Fe2—C21	1.78 (1)
In1—Fe1'	2.703 (2)	Fe2—C22	1.79 (1)
In1—Fe2	2.708 (1)	Fe2—C23	1.80 (1)
In1'—In1'	3.369 (2)	Fe2—C24	1.97 (1)
Fe1'—Fe1'	4.222	Fe2—C25	2.00 (1)
Fe16—Fe2'	2.616 (2)	O24—C24	1.18 (1)
Fe1—C13	1.77 (1)	O25—C25	1.16 (1)
Fe1—C11	1.782 (8)	O—C(ter) ^a	1.14 (1)
Fe1—C12	1.79 (1)		
Fe1—In1—Fe1'	102.82 (4)	C(ter)—Fe2—C(ter) ^a	98 (2)
Fe1—In1—Fe2	123.25 (4)	C21—Fe2—C24	169.6 (4)
In1—Fe1—In1'	77.18 (4)	C21—Fe2—C25	87.3 (4)
Fe1—In1—In1'	51.47 (4)	C21—Fe2—Fe2'	123.6 (3)
Fe1'—In1—Fe2	122.96 (4)	C21—Fe2—In1	85.7 (3)
Fe2'—Fe2—In1	61.12 (3)	Fe1—C—O(ter) ^a	178 (2)
Fe1'—In1—In1'	51.35 (4)	C22—Fe2—C24	90.8 (4)
Fe2—In1—Fe2'	57.77 (5)	C22—Fe2—C25	90.8 (4)
Fe2—In1—In1'	151.12 (3)	C22—Fe2—Fe2'	113.1 (3)
Fe2—C24—Fe2'	83.3 (5)	C22—Fe2—In1	174.1 (3)
Fe2—C25—Fe2'	81.6 (5)	C23—Fe2—C24	87.1 (4)
C13—Fe1—C11	98.8 (3)	C23—Fe2—C25	170.1 (4)
C13—Fe1—C12	98.6 (5)	C23—Fe2—Fe2'	122.9 (3)
C13—Fe1'—In1	93.2 (4)	C23—Fe2—In1	84.5 (3)
C13—Fe1—In1	170.4 (4)	C24—Fe2—C25	89.4 (4)
C11—Fe1—C11	155.5 (5)	C24—Fe2—Fe2'	48.3 (2)
C11—Fe1—C12	97.0 (3)	C24—Fe2—In1	84.3 (3)
C11—Fe1—In1	81.1 (2)	C25—Fe2—Fe2'	49.2 (2)
C11'—Fe1—In1	79.9 (3)	C25—Fe2—In1	85.9 (3)
C12'—Fe1—In1	168.2 (4)	Fe2—C—O(ter) ^a	175 (2)
C12—Fe1—In1	91.0 (4)	Fe2—C—O(br) ^a	138.8 (6)

^a indicates an average value.

The Fe atoms external to the ring can be likened to $\text{Fe}_2(\text{CO})_9$, where one CO has been replaced by a bridging In atom. The $\text{Fe}\text{---}\text{Fe}$ distance in $[(\text{C}_2\text{H}_5)_4\text{N}]_2[\text{In}_2\text{Fe}_6(\text{CO})_{24}]$ of 2.616 (2) Å is, as expected, significantly longer than that in $[\text{Fe}_2(\text{CO})_9]$ [2.523 (1) Å] (Cotton & Troup, 1974) due to the replacement of a CO group with a main-group functionality (Whitmire, Lagrone, Churchill, Fettinger & Biondi, 1984). In comparison, the

Fe—Fe distance in $\{[(C_6H_5)_3P]_2N\}_2[Tl_2Fe_6(CO)_{24}]\}$ is 2.610 (2) Å.

When compared to the Tl₂Fe₂ ring in $\{[(C_6H_5)_3P]_2N\}_2[Tl_2Fe_6(CO)_{24}]\}$, the In₂Fe₂ parallelogram shows a slightly wider Fe—In—Fe angle [Fe—In—Fe' = 102.82 (4); Fe—Tl—Fe = 100.89 (4)°], and a narrower In—Fe—In angle [In—Fe—In' = 77.18 (4); Tl—Fe—Tl = 79.11 (4)°] which probably reflects the size difference of the two main-group elements. The axial carbonyls on the ring Fe atoms are bent inward as in the thallium compound [C11—Fe1—C11' = 155.5 (5) and

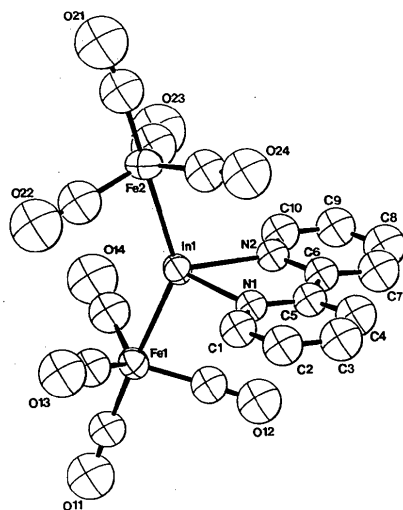


Fig. 3. ORTEP (Johnson, 1976) diagram of $[(bpy)InFe_2(CO)_8]^-$ with each carbonyl C atom labeled according to the O atom to which it is attached.

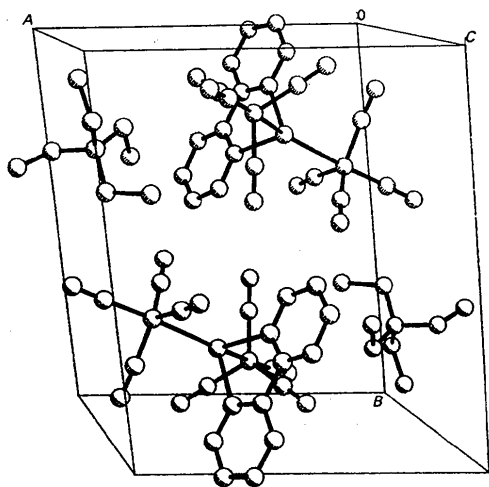


Fig. 4. Packing diagram of $[(C_2H_5)_4N][(bpy)InFe_2(CO)_8]$. Only the more highly populated α -C-atom positions of the cation are represented for clarity.

Table 3. Positional parameters and B_{eq} values for $[(bpy)InFe_2(CO)_8]^-$

$$B_{eq} = 8\pi^2/3(U_{11aa}^*{}^2 + U_{22bb}^*{}^2 + U_{33cc}^*{}^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha).$$

	x	y	z	B_{eq} (Å ²)
In1	0.31030 (5)	0.32995 (5)	0.25528 (3)	3.67 (2)
Fe1	0.5204 (1)	0.4630 (1)	0.18301 (7)	3.98 (4)
Fe2	0.2421 (1)	0.1395 (1)	0.34499 (8)	4.83 (4)
O11	0.7508 (9)	0.6341 (8)	0.1062 (6)	8.6 (2)
O12	0.3181 (8)	0.5775 (7)	0.1089 (5)	8.0 (2)
O13	0.6454 (9)	0.5149 (8)	0.3818 (6)	9.0 (2)
O14	0.521 (1)	0.2415 (9)	0.0724 (6)	9.9 (2)
O21	0.171 (1)	-0.084 (1)	0.4394 (7)	11.1 (3)
O22	0.516 (1)	0.239 (1)	0.4549 (7)	11.2 (3)
O23	0.203 (1)	0.019 (1)	0.1531 (8)	12.1 (3)
O24	0.031 (1)	0.2373 (9)	0.4170 (6)	9.9 (2)
C11	0.6577 (9)	0.5606 (8)	0.1351 (6)	5.2 (2)
C12	0.397 (1)	0.5302 (8)	0.1418 (6)	5.4 (2)
C13	0.593 (1)	0.4911 (8)	0.3022 (6)	5.7 (2)
C14	0.520 (1)	0.331 (1)	0.1201 (7)	6.5 (2)
C21	0.194 (1)	0.007 (1)	0.3993 (8)	7.5 (2)
C22	0.408 (1)	0.201 (1)	0.4060 (8)	7.4 (2)
C23	0.221 (1)	0.073 (1)	0.2322 (9)	8.0 (3)
C24	0.118 (1)	0.198 (1)	0.3846 (8)	7.0 (2)
N1	0.1915 (6)	0.4601 (5)	0.3127 (4)	3.9 (1)
N2	0.1136 (6)	0.3165 (5)	0.1483 (4)	4.2 (1)
C1	0.2316 (9)	0.5273 (8)	0.3989 (6)	5.3 (2)
C2	0.155 (1)	0.5959 (9)	0.4355 (7)	6.3 (2)
C3	0.038 (1)	0.598 (1)	0.3854 (8)	7.1 (2)
C4	-0.008 (1)	0.529 (1)	0.2974 (7)	6.7 (2)
C5	0.0726 (8)	0.4619 (7)	0.2621 (5)	4.6 (1)
C6	0.0331 (8)	0.3866 (7)	0.1697 (5)	4.5 (1)
C7	-0.078 (1)	0.387 (1)	0.1026 (7)	6.7 (2)
C8	-0.105 (1)	0.314 (1)	0.0172 (8)	7.7 (3)
C9	-0.026 (1)	0.2440 (9)	-0.0013 (7)	6.1 (2)
C10	0.085 (1)	0.2473 (8)	0.0633 (6)	5.5 (2)

C_{ax} —Fe— C_{ax} = 154.0 (6)°, respectively], a characteristic found in many main-group/transition-metal ring compounds (Ernst, Marks & Ibers, 1977; Gilmore & Woodward, 1972; Whitmire, Cassidy, Rheingold & Ryan, 1987).

An X-ray analysis of $[(C_2H_5)_4N][(bpy)InFe_2(CO)_8]$ shows that the asymmetric unit is composed of a disordered $[(C_2H_5)_4N]^+$ cation and a $[(bpy)InFe_2(CO)_8]^-$ anion in a 1:1 ratio. The anion consists of an In atom coordinated to two $[Fe(CO)_4]$ groups and to two N atoms of the Lewis base bipyridine with a distorted tetrahedral geometry. The $[Fe(CO)_4]$ groups are each arranged in a trigonal bipyramidal fashion with the In atom occupying an axial position. The equatorial CO's are tilted slightly toward the In atom. An ORTEP (Johnson, 1976) diagram of the anion is shown in Fig. 3, and a packing diagram in Fig. 4. Selected positional parameters and intramolecular distances and angles are given in Tables 3 and 4, respectively.

$[(C_2H_5)_4N][(bpy)InFe_2(CO)_8]$ has been synthesized from a structurally uncharacterized indium compound. This compound may be $[(C_2H_5)_4N]_2-[In_2Fe_4(CO)_{16}]$, an analogue of $[(C_2H_5)_4N]_2-[Tl_2Fe_4(CO)_{16}]$ (Whitmire, Cassidy, Rheingold & Ryan, 1987), as it was synthesized by the same

Table 4. Selected bond distances (Å) and angles (°) for [(bpy)InFe₂(CO)₈]⁻

In1—Fe1	2.545 (3)	N2—C10	1.35 (1)
In1—Fe2	2.552 (3)	C1—C2	1.37 (1)
In1—N1	2.334 (6)	C2—C3	1.33 (1)
In1—N2	2.335 (6)	C3—C4	1.38 (1)
Fe1—C ^a	1.72 (1)	C4—C5	1.39 (1)
Fe2—C ^a	1.71 (2)	C5—C6	1.46 (1)
O—C ^a	1.19 (2)	C6—C7	1.40 (1)
N1—C1	1.35 (1)	C7—C8	1.38 (1)
N1—C5	1.34 (1)	C8—C9	1.32 (1)
N2—C6	1.35 (1)	C9—C10	1.36 (1)
N2—In1—N1	69.5 (2)	N1—In1—Fe2	107.6 (2)
N2—In1—Fe1	106.0 (2)	Fe1—In1—Fe2	139.75 (7)
N2—In1—Fe2	105.8 (2)	Fe—C—O ^a	176 (1)
N1—In1—Fe1	106.3 (2)	C21—Fe2—In1	176.8 (4)
C(ax)—Fe1—C(eq) ^a	97 (2)	C11—Fe1—In1	176.3 (3)
C(eq)—Fe1—C(eq) ^a	118 (2)	C(eq)—Fe1—In1 ^a	83 (3)
C(ax)—Fe2—C(eq) ^a	97.0 (7)	C(eq)—Fe2—In1 ^a	83 (2)
C(eq)—Fe2—C(eq) ^a	118 (3)	C6—N2—C10	119.5 (7)
C5—N1—In1	119.0 (5)	C6—N2—In1	118.5 (5)
C5—N1—C1	118.2 (6)	C10—N2—In1	121.8 (5)
N2—C10—C9	122.1 (8)	N1—C1—C2	122.2 (8)
C1—N1—In1	122.5 (5)	C—C—C(ring) ^a	120 (1)
N1—C5—C4	121.2 (7)	C4—C5—C6	122.7 (8)
N1—C5—C6	116.1 (7)	C7—C6—C5	124.3 (8)
N2—C6—C7	119.0 (7)	N2—C6—C5	116.7 (7)

^a indicates an average value.

method, has a similar IR spectrum and shows similar chemical reactivity. This indium compound forms several Lewis base adducts with 1,10-phenanthroline, bpy, ethylenediamine, diethylenetriamine and TMEDA, as does the thallium compound (Cassidy & Whitmire, 1989). In isostructural [(C₂H₅)₄N]-[(bpy)TlFe₂(CO)₈], the Tl—Fe and the Tl—N distances are 2.568 (2) and 2.61 (1) Å, respectively, whereas in [(C₂H₅)₄N][(bpy)InFe₂(CO)₈] the In—Fe distances are 2.545 (3) and 2.552 (3) Å and the In—N distances are 2.334 (6) and 2.335 (6) Å. The shorter In—N distances are probably the result of the smaller covalent radius and the increased electronegativity of the In atom *versus* the Tl atom.

The In—N distances in [(C₂H₅)₄N][(bpy)InFe₂(CO)₈] compare favorably with several compounds having indium—Lewis base interactions, including [InCl₂(acac)(bpy)] [acac = acetylacetonate; $d_{\text{In—N}} = 2.276$ (4) and 2.299 (4) Å] (Contreras, Einstein & Tuck, 1974), [(CH₃)₂NCH₂C₆H₄]₂InCl [$d_{\text{In—N}} = 2.442$ (3) and 2.482 (2) Å] (Khan, Steevensz, Tuck, Noltes & Corfield, 1980), [Cl₂In(O₂CC₆H₅)(C₅H₅N)₂] [$d_{\text{In—N}} = 2.250$ (5) and 2.300 (6) Å] (Khan, Peppe & Tuck, 1983) and InBr₃.3C₅H₅N [$d_{\text{In—N}} = 2.32$ (3), 2.31 (2) and 2.28 (3) Å] (Small & Worrall, 1982). The N—In—N angle [69.5 (1)°] in [(C₂H₅)₄N]-[(bpy)InFe₂(CO)₈] is in good agreement with the N—In—N angle found in [InCl₂(acac)(bpy)] [71.7 (1)°]; the bipyridine ligand parameters are also very nearly the same.

Upon comparison of the In—Fe bond lengths in [(C₂H₅)₄N][(bpy)InFe₂(CO)₈] {av. 2.549 (5) Å; e.s.d.'s

of average values are calculated with the scatter formula: $\sigma = [\sum_{i=1}^N (d_i - d)^2 / (N - 1)]^{1/2}$ and the In—Fe distance in [(C₂H₅)₄N]₂[In₂Fe₆(CO)₂₄], external to the ring [2.708 (1) Å], one notices that the In—Fe distance in [(C₂H₅)₄N]₂[In₂Fe₆(CO)₂₄] is approximately 0.16 Å longer than in [(C₂H₅)₄N]-[(bpy)InFe₂(CO)₈]. Formally, the In—Fe distances in both compounds may be considered single bonds since the In atoms each achieve a filled octet of electrons. Therefore, the longer In—Fe bond lengths in [(C₂H₅)₄N]₂[In₂Fe₆(CO)₂₄] are probably due to steric crowding.

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References

- BURLITCH, J. M., LEONOWICZ, M. E., PETERSEN, R. B. & HUGHES, R. E. (1979). *Inorg. Chem.* **18**, 1097–1105.
- CASSIDY, J. M. & WHITMIRE, K. H. (1989). *Inorg. Chem.* **28**, 1432–1435.
- CONTRERAS, J. G., EINSTEIN, F. W. B. & TUCK, D. G. (1974). *Can. J. Chem.* **52**, 3793–3798.
- COTTON, F. A. & TROUP, J. M. (1974). *J. Chem. Soc. Dalton Trans.* pp. 800–802.
- CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, p. 71 (scattering factors) and p. 148 (anomalous dispersion). Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- ERNST, R. D., MARKS, T. J. & IBERS, J. A. (1977). *J. Am. Chem. Soc.* **99**, 2090–2098, 2098–2107.
- GILMORE, C. J. (1983). *MITHRIL. A Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. Univ. of Glasgow, Scotland.
- GILMORE, C. J. & WOODWARD, P. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1387–1392.
- HSIEH, A. T. T. & MAYS, M. J. (1971). *Inorg. Nucl. Chem. Lett.* **7**, 223–225.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KHAN, M. A., PEPPE, C. & TUCK, D. G. (1983). *Acta Cryst.* **C39**, 1339–1342.
- KHAN, M. A., PEPPE, C. & TUCK, D. G. (1984). *Can. J. Chem.* **62**, 601–605.
- KHAN, M. A., STEEVENSZ, R. C., TUCK, D. G., NOLTES, J. G. & CORFIELD, P. W. R. (1980). *Inorg. Chem.* **19**, 3407–3411.
- Molecular Structure Corporation (1988a). *CONTROL* (4:1:0). Program for Data Collection. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988b). *TEXSAN. TEXRAY Structure Analysis Package*. Version 2.1. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.
- PREUT, H. & HAUPT, H.-J. (1979). *Acta Cryst.* **B35**, 2191–2192.
- RUFF, J. K. (1968). *Inorg. Chem.* **7**, 1499–1503.
- SHELDRICK, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
- SMALL, R. W. H. & WORRALL, I. J. (1982). *Acta Cryst.* **B38**, 932–934.
- WHITMIRE, K. H., CASSIDY, J. M., RHEINGOLD, A. L. & RYAN, R. R. (1987). *Inorg. Chem.* **27**, 1347–1353.
- WHITMIRE, K. H., LAGRONE, C. B., CHURCHILL, M. R., FETTINGER, J. C. & BIONDI, L. V. (1984). *Inorg. Chem.* **23**, 4227–4232.