

(Ribár, Kozmidis-Petrović & Leovac, 1980) and (*o*-phenanthroline)(salicylaldehyde *S*-methylisothiosemicarbazato)copper(II) nitrate (Petrović, Carić, Leovac & Canić, 1979). Bond distances and angles in the chelating ligand are in good agreement with those found in these compounds. It is worth noting that the Co(1)–N(1) distance is slightly (but not significantly, $\Delta/\sigma = 1.83$) shorter than Co(1)–N(3), and the same difference has been observed for the other transition-metal complexes of *S*-methylisothiosemicarbazones.

As a consequence of chelation five- and six-membered metallocycles are formed in which the displacements from the best planes do not exceed 0.08 Å. The dihedral angle between these planes is 8.0°. The angles between the benzene ring and the six- and five-membered metallocycles are 2.6 and 10.3° respectively. The py(1) and py(3) planes are approximately perpendicular to each other and to the best plane through N(1), N(3), N(5) and O. The py(2) ring forms an angle of 34.5° with this plane and it is nearly perpendicular to the plane through N(1), N(4), N(6) and O. The py(4) plane is approximately a symmetry plane for the Cl(2)–Co(2)–Cl(3) angle, while Cl(1) is located closely to this plane. The torsion angle C(29)–N(7)–Co(2)–Cl(1) is 11 (1)°.

The imido form for the thiosemicarbazide fragment [$\dots\text{N}=\text{N}(\text{H})-\text{C}(\text{NH})-\text{SCH}_3$] of the ligand, characteristic for all *S*-methyl derivatives of thiosemicarbazides and thiosemicarbazones (Divjaković, Ribár, Leovac & Gerbeleu, 1981), has been confirmed. The double bond is delocalized along N(1)–C(1)–N(2) as indicated by the values of the distances C(1)–N(1) and C(1)–N(2) which are practically equal and intermediate between single and double bonds. The imido

form of the ligand is also substantiated by the positions of the H atoms: in the difference Fourier map around N(1) there is only one maximum which may correspond to an H atom. Furthermore, there is a maximum at a distance of 0.97 Å from N(2) which can be ascribed to an H atom, supposedly transferred, during the complex formation, from the N(1)H₂ group to the hydrazine N(2).

References

- BIYSKIN, V. N., GERASIMOV, V. I. & BELOV, N. V. (1981). *Sov. Phys. Crystallogr.* **26**, 323–331.
- BKOUCHE-WAKSMAN, I. & L'HARIDON, P. (1977). *Acta Cryst.* **B33**, 11–21.
- DAY, M. C. & SELBIN, J. (1969). In *Theoretical Inorganic Chemistry*. New York: Reinhold.
- DIVJAKOVIĆ, V., RIBÁR, B., LEOVAC, V. M. & GERBELEU, N. V. (1981). *Z. Kristallogr.* **154**, 83–94.
- GEARY, W. J. (1971). *Coord. Chem. Rev.* **7**, 81.
- GERBELEU, N. N., TURTE, K. I., CANIĆ, V. D., LEOVAC, V. M. & ARION, V. B. (1980). *Koord. Khim.* **6**, 446–448 (in Russian).
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LAING, M. & CARR, G. (1975). *Acta Cryst.* **B31**, 2683–2684.
- LEOVAC, V. M. (1978). PhD Thesis, Institute of Chemistry, Faculty of Sciences, Univ. of Novi Sad, Yugoslavia.
- LEOVAC, V. M., GERBELEU, N. N. & REVENKO, M. D. (1978). *Zh. Neorg. Khim.* **23**, 1272–1274.
- PETROVIĆ, D., CARIĆ, S., LEOVAC, V. M. & CANIĆ, V. D. (1979). *Cryst. Struct. Commun.* **8**, 617–620.
- RIBÁR, B., KOZMIDIS-PETROVIĆ, A. & LEOVAC, V. M. (1980). *Cryst. Struct. Commun.* **9**, 1237–1241.
- VANCE, T. B. JR, HOLT, E. M., PIERNOT, C. S. & HOLT, S. L. (1980). *Acta Cryst.* **B36**, 150–153.

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Low-Temperature Crystallization of Orthorhombic Ferrocene: Structure Analysis at 98 K

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Abstract

Single crystals of the new low-temperature modification of ferrocene, isomorphous with ruthenocene, have been obtained by crystallization at temperatures below 110

K. Once formed, the crystals can be warmed to about 275 K before transformation to the monoclinic phase occurs. The structure of orthorhombic ferrocene has been determined at 98 K: $\text{Fe}(\text{C}_5\text{H}_5)_2$, $M_r = 186.0$, $a = 6.987$ (6), $b = 8.995$ (7), $c = 12.196$ (5) Å, $U =$

766.5 \AA^3 , space group *Pnma*, $Z = 4$, $D_c = 1.61 \text{ Mg m}^{-3}$. $R = 0.027$ for 379 observed reflexions ($I \geq 3\sigma_I$). The ferrocene molecules are exactly eclipsed (molecular symmetry D_{5h}) with average Fe–C = 2.059 \AA and C–C = 1.431 \AA , close to the values found for triclinic ferrocene at approximately the same temperature [Seiler & Dunitz (1979). *Acta Cryst.* B35, 2020–2032]. The vibrational amplitudes of the atoms are smaller than in triclinic ferrocene and approximately equal to those in isomorphous ruthenocene [Seiler & Dunitz (1980). *Acta Cryst.* B36, 2946–2950].

Introduction

At 164 K ferrocene [bis(cyclopentadienyl)iron] undergoes a phase transition (Edwards, Kington & Mason, 1960). The monoclinic high-temperature (HT) phase (space group $P2_1/a$, $Z = 2$) is disordered (Seiler & Dunitz, 1979a; Takusagawa & Koetzle, 1979). Below 164 K the structure is triclinic, and all three crystal axes of the monoclinic (HT) cell are doubled. Triclinic crystals produced by cooling from room temperature through the phase transition are invariably multiple twins, but an untwinned crystal of the triclinic low-temperature (LT) phase (space group $F\bar{1}$, $Z = 16$) could be produced below 164 K by sublimation in an evacuated capillary tube and its structure determined (Seiler & Dunitz, 1979b). The two independent $\text{Fe}(\text{C}_5\text{H}_5)_2$ molecules have almost regular pentagonal cyclopentadienyl rings and show virtual D_5 symmetry, the rings being rotated by about 9° from the eclipsed orientation.

Ogasahara, Sorai & Suga (1979) have described a new LT phase with a lower molar heat capacity than that found for the triclinic LT phase. The transformation into this new phase was accomplished by cooling large crystals of ferrocene (crystal size about 1 mm^3) below 164 K until they disintegrated and then annealing at about 190 K for several hours. Ogasahara *et al.* (1979) concluded that the new LT phase is the thermodynamically stable phase below 242 K and that the well known transition at 164 K is between metastable phases.

Similar observations were made by Bézar, Calvarin, Weigel, Chhor & Pommier (1980), who, in addition, showed by powder diffractometry that the new LT phase is isomorphous with the orthorhombic structure of ruthenocene (Hardgrove & Templeton, 1959; Seiler & Dunitz, 1980b).

We have now made further crystallization experiments at temperatures ranging from 240 to about 90 K and have succeeded in obtaining single crystals of the orthorhombic phase and in determining its structure at 98 K.

Preliminary results for the orthorhombic modification of nickelocene [$\text{Ni}(\text{C}_5\text{H}_5)_2$] are also discussed.

Experimental

All X-ray measurements were made on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$) and a modified Nonius cooling system.

Low-temperature crystallization experiments

Commercially available ferrocene was purified by repeated vacuum sublimation. For each experiment a small amount was dissolved in ethanol or 1-propanol, and enclosed in a glass capillary ($\varnothing 0.3 \text{ mm}$, length about 20 mm), which was mounted on the diffractometer and cooled by a jet of cold nitrogen. In this way it was possible to obtain single crystals of ferrocene at temperatures of approximately 245, 215, 190 and 160 K (from ethanol), and 110 and 90 K (from 1-propanol). The crystallization process could be observed directly through a telescope, and once crystals were formed they were investigated by diffractometry without rewarming.

In agreement with our earlier results with crystallization from the vapour (Seiler & Dunitz, 1979b), we found that at temperatures above 164 K only the monoclinic modification was obtained and at 160 K only the triclinic. Although the range of stability of the new LT phase is said to extend from 0 to 242 K (Ogasahara *et al.*, 1979; Bézar *et al.*, 1980), we were never able to obtain a single crystal of this phase from solution at temperatures above about 110 K. At this temperature, however, crystallization from solution produced a mixture of small greenish and brownish plates, which we could identify as the old triclinic phase and the new orthorhombic one, respectively. Only at still lower temperatures, *e.g.* at about 90 K, did we obtain crystals belonging exclusively to the new phase. There is still the possibility that crystals of the new phase could be grown at higher temperatures if the right conditions can be found.

Although the triclinic phase is metastable through its range of existence, single crystals (size $0.15\text{--}0.2 \text{ mm}$; mosaic spread $<0.3^\circ$) of this form, grown below 164 K, can be kept for weeks and possibly indefinitely at temperatures between 100 and 164 K. Also, the mosaic spread of such crystals is hardly affected by rapid cooling (up to 5 K s^{-1}), in contrast to specimens obtained by cooling the monoclinic HT form through the phase transition.

Crystal data

The crystal data are shown in the *Abstract*; space group *Pnma* was assigned from systematic absences and by analogy to ruthenocene [$a = 7.009$, $b = 8.819$, $c = 12.796 \text{ \AA}$ at 101 K (Seiler & Dunitz, 1980b)].

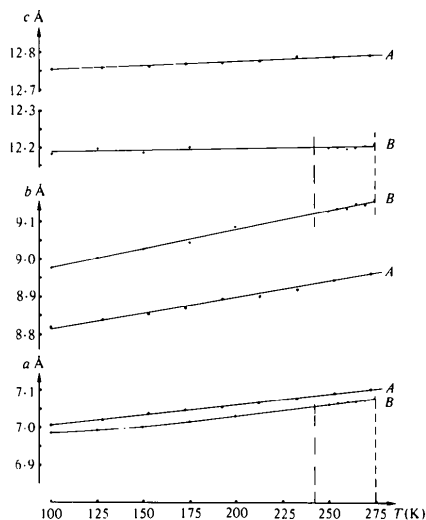


Fig. 1. Temperature dependence of lattice parameters in the range 100 to 275 K: (A) ruthenocene, (B) ferrocene. The orthorhombic crystals of ferrocene are reported to transform to the monoclinic form at 242 K (Ogasahara *et al.*, 1979; Bézar *et al.*, 1980) but our crystal did not transform until 275 K.

The temperature dependence of the cell dimensions is also very similar to that of ruthenocene, as shown in Fig. 1. These results agree well with those obtained by powder diffractometry by Bézar *et al.* (1980).

The temperature at which the irreversible orthorhombic–monoclinic transformation occurs varies somewhat from crystal to crystal, but most show considerable hysteresis. As indicated in Fig. 1, diffractometer measurements on one crystal could be made up to 275 K, which is 33 K higher than the reported phase transition.

Structure analysis and refinement

A complete set of intensity measurements was obtained at 98 K with a crystal $0.12 \times 0.12 \times 0.08$ mm ($\sin \theta/\lambda$

limit 0.57 \AA^{-1} , 634 independent reflexions, 379 with $I \geq 3\sigma_r$). Absorption corrections were not applied ($\mu \sim 1.9 \text{ mm}^{-1}$).

As starting-point for least-squares refinement we simply took the atom coordinates from the ruthenocene structure at 101 K (Seiler & Dunitz, 1980*b*). Preliminary isotropic refinement (without H atoms) converged at $R = 0.055$; subsequent refinement, anisotropic for Fe and C, H atoms at calculated positions (C–H = 1.08 \AA , C–H direction along bisector of the CCC angle, $U_{\text{iso}} = 0.025 \text{ \AA}^2$) converged at $R = 0.027$, $R_w = 0.019$ using standard scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1968) and a modified weighting system (Dunitz & Seiler, 1973) with $r = 1.5 \text{ \AA}^2$, but ignoring dispersion corrections. Final positional and vibrational parameters are in Table 1.*

Comparison with ruthenocene

Bond distances in the ferrocene molecule are given in Table 2. As in the ruthenocene crystal (Seiler & Dunitz, 1980*b*), the molecule lies on a crystallographic mirror plane passing through Fe, C(1), and C(4), so that the two cyclopentadienyl rings are exactly eclipsed. Again, as in ruthenocene, the two symmetry-independent rings are almost regular pentagons, parallel to one another, and equidistant from the metal atom, to make the effective molecular symmetry D_{5h} . Apart from the metal–C distances [mean 2.056 \AA (corrected 2.059 \AA)], which are about 0.13 \AA shorter in ferrocene than in ruthenocene, the two structures are practically the same. This similarity extends even to the atomic vibrational parameters, which are less accurately determined than those in ruthenocene at 101 K

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36714 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and vibrational parameters ($\text{\AA}^2 \times 10^4$) (with *e.s.d.*'s in parentheses) obtained from the X-ray analysis of orthorhombic ferrocene at 98 K

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	2355 (1)	2500	5040 (1)	76 (3)	101 (3)	60 (3)	0	−10 (7)	0
C(1)	5018 (9)	2500	5756 (5)	131 (30)	225 (38)	134 (34)	0	−38 (29)	0
C(2)	2238 (6)	3298 (6)	6624 (3)	142 (25)	140 (24)	78 (20)	8 (27)	−68 (21)	−20 (20)
C(3)	3954 (6)	3786 (6)	6084 (3)	131 (21)	147 (27)	101 (25)	−40 (21)	−38 (19)	1 (19)
C(4)	2716 (10)	2500	3362 (4)	169 (39)	220 (37)	64 (26)	0	−27 (33)	0
C(5)	−17 (6)	3291 (4)	4237 (3)	125 (19)	128 (22)	82 (22)	12 (22)	−51 (20)	13 (21)
C(6)	1677 (6)	3781 (5)	3701 (4)	160 (23)	142 (28)	88 (23)	−17 (21)	−13 (19)	19 (22)
	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(1)	6380	2500	5339	250	H(4)	4062	2500	2925	250
H(2)	1143	4004	6968	250	H(5)	−1112	3997	4584	250
H(3)	4368	4928	5949	250	H(6)	2099	4923	3571	250

Table 2. *Bond distances* (Å)

E.s.d.'s are about 0.005 Å for Fe—C, and 0.006 Å for C—C distances. Values in parentheses are corrected for librational motion.

Fe—C(1)	2.055 (2.058)	C(2')—C(2)	1.435 (1.438)
Fe—C(2)	2.062 (2.065)	C(2)—C(3)	1.437 (1.439)
Fe—C(3)	2.051 (2.054)	C(3)—C(1)	1.432 (1.435)
Fe—C(4)	2.063 (2.065)	C(5')—C(5)	1.424 (1.426)
Fe—C(5)	2.053 (2.055)	C(5)—C(6)	1.421 (1.425)
Fe—C(6)	2.055 (2.057)	C(6)—C(4)	1.423 (1.426)
Fe—C (mean)	2.056 (2.059)	C—C (mean)	1.429 (1.431)

but are not significantly different from them. Thus the results of the thermal-motion analysis provided in the ruthenocene paper also apply *mutatis mutandis* to the present one; in particular, the somewhat greater apparent librational motion of ring (I) [C(1)—C(3)] than of ring (II) [C(4)—C(6)]. As indicated in Table 2, the mean C—C distance in ring (I) is 0.012 (6) Å longer than in ring (II), but we tend not to ascribe too much significance to this.

The packing is the same as in isomorphous ruthenocene with allowance for the slightly smaller molecular volume (192 Å³ compared with 197 Å³ in ruthenocene).

Comparison with triclinic ferrocene

In the triclinic structure (Seiler & Dunitz, 1979*b*) the asymmetric unit consists of two ferrocene molecules which both deviate by about 9° from the exact eclipsed orientation of the rings. The average Fe—C distance at 101 K is 2.052 Å (corrected for libration), very slightly shorter than the distance in the orthorhombic structure; the average C—C distances in the two structures are practically the same, 1.433 and 1.431 Å (both corrected).

The atomic vibration parameters (measured at nearly the same temperature) are, however, markedly smaller in the orthorhombic crystal than in the triclinic one (compare Table 1 with Table 3 of Seiler & Dunitz, 1979*b*). For example, the largest eigenvalue of the librational tensor *L* is about 8 deg² in the orthorhombic structure and about 28 deg² in the triclinic one, both librations being roughly about the molecular fivefold symmetry axis. The molecular volume is slightly smaller in the orthorhombic structure throughout the measured temperature range; at around 100 K the values are 192 Å³ and 195 Å³. These differences in vibrational amplitudes and molecular volume both support the view that at this temperature the new orthorhombic crystal is the thermodynamically stable form, in agreement with the results of Ogasahara *et al.* (1979) and Bélar *et al.* (1980).

Discussion

Our experiments show that ferrocene can be crystallized from solution in the monoclinic, triclinic, and orthorhombic crystal modifications, depending on the temperature. Although the orthorhombic form is thermodynamically stable up to 242 K, crystallization of this phase from solution occurred in our experiments only at much lower temperatures (110 K or less). At higher temperatures the other two crystal forms were obtained in spite of their thermodynamic metastability.

It is clear that for ferrocene the crystallization process is under kinetic rather than thermodynamic control, the rate-determining step being the formation of nuclei. In this respect, the free energy of nucleation is analogous to the activation energy for crystal formation; it can well happen that a metastable crystal is associated with a smaller energy of nucleation than the stable modification and is hence formed faster. It seems in our experiments that only at temperatures around 110 K does nucleation of the orthorhombic modification begin to predominate. Once formed, however, the orthorhombic crystals can be warmed to temperatures some 20 K, or more, above the orthorhombic—monoclinic transition point at 242 K, in contrast to the behaviour of the triclinic and monoclinic crystals which show very little or no hysteresis at the order—disorder transition at 164 K.

What about the other metallocenes, such as nickelocene, cobaltocene and magnesocene? Can they also be obtained in orthorhombic modifications isomorphous with ruthenocene? In preliminary experiments with nickelocene, we have been able to produce orthorhombic crystals, together with monoclinic ones, from solution at temperatures around 175 K, but only after seeding with ruthenocene. The crystals obtained so far still contain 20–25% ruthenocene, and all our attempts to grow a pure single crystal of orthorhombic nickelocene between 90 K and room temperature have failed up till now.

Gas-phase electron-diffraction studies have shown that whereas the free Ni(C₅H₅)₂ molecule shows nearly free rotation of the cyclopentadienyl rings (Hedberg & Hedberg, 1970), Fe(C₅H₅)₂ prefers the eclipsed orientation by about 4 kJ mol⁻¹ (Haaland & Nilsson, 1968). This difference between the properties of the free molecules is probably largely responsible for the difference in behaviour of the monoclinic crystals of the two substances, ferrocene transforming at 164 K into the triclinic structure with nearly eclipsed molecules, nickelocene remaining monoclinic at least down to 100 K (Seiler & Dunitz, 1980*a*) and probably down to 5 K (Calvarin & Weigel, 1976). In the same way, it seems very likely that the difference between the stability ranges of the orthorhombic structures of ruthenocene and ferrocene is also attributable to a similar difference

in molecular properties. No experimental evidence for the energy barrier in $\text{Ru}(\text{C}_5\text{H}_5)_2$ seems to be available, but a theoretical study by Carter & Murrell (1980) indicates that the stabilization of the eclipsed orientation is about 2 kJ mol^{-1} greater than in $\text{Fe}(\text{C}_5\text{H}_5)_2$.

This kind of dependence of crystal structure on the preferred orientation and energy barrier of the free molecules is strongly supported by recent lattice-energy calculations by Brock (1981). For a crystal built from metallocene molecules with free rotation of the rings but with variable metal–C distances and atomic charges, the monoclinic structure with centrosymmetric molecules is more stable than the orthorhombic one with eclipsed molecules by several kJ mol^{-1} for all reasonable values of the parameters. Any observed energetic preference for the orthorhombic structure would then have to be attributed to an intrinsic preference of the free molecules for the eclipsed orientation.

References

- BÉRAR, J. F., CALVARIN, G., WEIGEL, D., CHHOR, K. & POMMIER, C. (1980). *J. Chem. Phys.* **73**, 438–441.
 BROCK, C. P. (1981). Unpublished results.
 CALVARIN, G. & WEIGEL, D. (1976). *J. Appl. Cryst.* **9**, 212–215.
 CARTER, S. & MURRELL, J. M. (1980). *J. Organomet. Chem.* **192**, 399–408.
 DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* **B29**, 589–595.
 EDWARDS, J. W., KINGTON, G. L. & MASON, R. (1960). *Trans. Faraday Soc.* **56**, 660–667.
 HAALAND, A. & NILSSON, J. E. (1968). *Acta Chem. Scand.* **22**, 2653–2670.
 HARDGROVE, G. L. & TEMPLETON, D. H. (1959). *Acta Cryst.* **12**, 28–32.
 HEDBERG, L. & HEDBERG, K. (1970). *J. Chem. Phys.* **53**, 1228–1234.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., Table 3.3.1A. Birmingham: Kynoch Press.
 OGASAHARA, K., SORAI, M. & SUGA, H. (1979). *Chem. Phys. Lett.* **68**, 457–460.
 SEILER, P. & DUNITZ, J. D. (1979a). *Acta Cryst.* **B35**, 1068–1074.
 SEILER, P. & DUNITZ, J. D. (1979b). *Acta Cryst.* **B35**, 2020–2032.
 SEILER, P. & DUNITZ, J. D. (1980a). *Acta Cryst.* **B36**, 2255–2260.
 SEILER, P. & DUNITZ, J. D. (1980b). *Acta Cryst.* **B36**, 2946–2950.
 TAKUSAGAWA, F. & KOETZLE, T. F. (1979). *Acta Cryst.* **B35**, 1074–1081.

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Clathrate Inclusion Compounds of Bis(isothiocyanato)- tetrakis(4-methylpyridine)nickel(II).

V.* Bis(isothiocyanato)tetrakis(4-methylpyridine)nickel(II)–Naphthalene (1:2)

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Abstract

The structure of $[\text{Ni}(\text{C}_6\text{H}_7\text{N})_4(\text{NCS})_2] \cdot 2\text{C}_{10}\text{H}_8$ has been determined by X-ray diffraction and refined to $R = 0.065$ for 4402 observed reflections. A layer-type packing of host $\text{Ni}(\text{4-methylpyridine})_4(\text{NCS})_2$ molecules occurs. Three symmetrically independent guest naphthalene molecules occupy cavities between these layers. Crystal data: $\text{C}_{26}\text{H}_{28}\text{N}_6\text{NiS}_2 \cdot 2\text{C}_{10}\text{H}_8$, $M_r = 803.7$, is monoclinic, space group $C2/c$, with $a = 16.266$ (14), $b = 16.456$ (15), $c = 31.929$ (11) Å, $\beta =$

89.26 (8)°, $U = 8545 \text{ Å}^3$, $D_c = 1.249 \text{ Mg m}^{-3}$, $Z = 8$, $F(000) = 3376$, $\mu(\text{Cu } K\alpha) = 1.74 \text{ mm}^{-1}$.

Introduction

$\text{Ni}(\text{4-MePy})_4(\text{NCS})_2^\dagger$ clathrates with isomeric 2- or 1-methylnaphthalenes as guest components (Lipkowski, Sgarabotto & Andreotti, 1980, 1982) crystallize with layer-type molecular packing. Substitution of the guest with a smaller molecule, like

* Part IV: Lipkowski & Andreotti (1982).

† 4-MePy = 4-methylpyridine ($\text{MeC}_4\text{H}_4\text{N}$).