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The Structure of Nickelocene at Room Temperature and at 101 K

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Abstract

Nickelocene is monoclinic at room temperature (RT) and at 101 K [a = 10·735 (3), b = 7·868 (3), c = 5·910 (2) Å, β = 121·42 (6)° at 293 K; a = 10·461 (9), b = 8·041 (9), c = 5·757 (5), β = 123·53 (7)° at 101 K; space group $P2_1/a$, Z = 2]. At RT nickelocene is isostructural with monoclinic ferrocene [Seiler & Dunitz (1979). *Acta Cryst.* B**35**, 1068–1074] but, in contrast to ferrocene, there is no phase change to a triclinic structure on cooling. Structure analyses at both temperatures show essentially the same molecular structure with an appreciable decrease in thermal motion on cooling. (At RT R = 0·034, and at 101 K R = 0.028.) At 101 K the centrosymmetric $Ni(C_5H_5)_2$ molecules have almost regular pentagonal cyclopentadienyl rings (C—C, 1·423 Å) and have approximate D_{5d} symmetry (staggered rings) with mean Ni—C = 2·185 Å. Thermal-motion analysis of the 101 K results shows that the librational motion of the cyclopentadienyl rings is larger than in triclinic ferrocene at the same temperature [Seiler & Dunitz (1979). *Acta Cryst.* B**35**, 2020–2032] and approximately equal to that in ferrocene at 135 K. The crystal packing of nickelocene shows none of the short H···H contacts present in the triclinic ferrocene structure.

Introduction

At 164 K ferrocene [bis(cyclopentadienyl)iron] undergoes a transition from a disordered monoclinic phase (C^5_{2h}, Z = 2) to an ordered triclinic phase (C^1_i, Z = 4) (Seiler & Dunitz, 1979*a*,*b*). Pfab & Fischer (1953) showed that ferrocene and nickelocene [bis(cyclopentadienyl)nickel] are isomorphous at room temperature, but no crystal structure analysis of the latter has been reported. Calvarin & Weigel (1976) measured the powder diffraction of nickelocene in the temperature range 5–295 K and concluded, from the temperature dependence of the cell parameters, that an order–disorder transition occurs in the range 170–240 K. However, specific-heat measurements are not entirely unambiguous concerning this point. Whereas Azokpota, Calvarin & Pommier (1976) find a rather broad peak in the specific-heat curve, roughly in the expected temperature range, this feature is not reproduced by later measurements by Rabinovich, Nistratov, Sheiman & Burchalova (1978), who find only 'a poorly defined but distinctive hump' in the specific-heat curve between 100 and 190 K. This behaviour is in marked contrast to that of ferrocene, which shows a sharp specific-heat peak at 164 K and a secondary peak a few degrees higher (Edwards, Kington & Mason, 1960; Edwards & Kington, 1962; Calvarin & Weigel, 1976). The apparent similarity between the RT structures of ferrocene and nickelocene and the apparent differences in the heat-capacity behaviour have led us to carry out single-crystal X-ray diffraction studies on nickelocene, at RT and also at 100 K.

Experimental

All X-ray measurements were made on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, λ = 0·71069 Å) and a slightly modified Nonius low-temperature device.

Single crystals of nickelocene could be obtained by sublimation of a commercial sample, but they were extremely fragile. Cell dimensions (and their dependence on temperature) appeared to vary slightly but significantly from one crystal specimen to another. The intensities were therefore collected at room temperature (293 K, RT) and at 101 K (LT) from the same crystal specimen (~0·2 mm on edge) which had previously been enclosed in epoxy resin.

Cell dimensions measured for this crystal were:

	a (Å)	b (Å)	c (Å)	β (°)
293 K	10·735 (3)	7·868 (3)	5·910 (2)	121·42 (6)
101 K	10·461 (9)	8·041 (9)	5·757 (5)	123·53 (7).

The expansion of b on cooling is remarkable. Fig. 1 shows that the temperature dependence of b is anomalous in that the thermal-expansion coefficient along b is *negative* throughout the temperature range covered with a distinct change of slope around 180 K. Our observations agree with the powder-diffractometry results of Calvarin & Weigel (1976), who showed that

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the anomalous thermal contraction along b persists down to about 20 K, below which temperature the change in cell dimensions becomes imperceptible.

On cooling the crystals to about 175 K, typical reflexion profiles broadened irreversibly to a maximum width of 1·5–2° but remained roughly constant on further cooling.

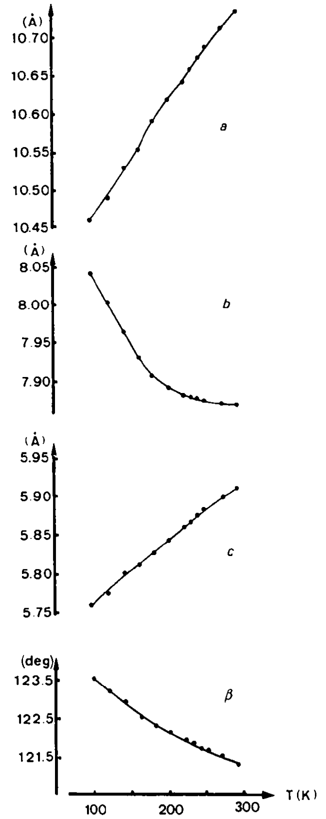

Fig. 1. Temperature dependence of nickelocene lattice parameters in the range 100–300 K.

Intensity measurements were made, first at 101 K (sin θ/λ limit 0·60 Å^{-1}, 771 independent reflexions, 616 with $I \geq 1{\cdot}5\sigma_I$) and then at RT (sin θ/λ limit 0·64 Å^{-1}, 837 independent reflexions, 557 with $I \geq 1{\cdot}5\sigma_I$). The intensities of two standard reflexions did not change during the LT measurements but decreased by 7% during the RT measurements. Intensities were converted to relative $|F|$ values in the usual way, but absorption corrections were not applied ($\mu \sim 2{\cdot}2$ mm^{-1}).

The RT ferrocene coordinates (Seiler & Dunitz, 1979*a*) were used as starting-point for refinement of the nickelocene RT data (final $R = 0{\cdot}034$). The resulting coordinates were used in turn as starting-point for refinement of the 101 K data (final $R = 0{\cdot}028$). Both analyses were based on scattering factors for neutral atoms taken from *International Tables for X-ray Crystallography* (1974) and a modified weighting system (Dunitz & Seiler, 1973) with $r = 5{\cdot}0$ Å^2 was employed. Difference maps calculated with both data sets showed weak peaks near expected H positions. For the LT analysis H positions were refined (isotropic U) but calculated H positions (C—H direction along bisector of CCC angle, C—H = 1·08 Å) were used in the final stages of the RT analysis.

The F_o synthesis calculated for reflections with $h + k$ even (all coefficients taken as positive) is independent of any assumptions concerning the light atoms. This synthesis showed five distinct peaks in a pentagonal arrangement at positions close to those obtained by the least-squares refinement. The alternative model with freely rotating cyclopentadienyl rings can therefore be rejected.

Table 1. *Atomic positions and vibrational parameters* (*all* ×10^4) (*with e.s.d.'s in parentheses*) *obtained from the X-ray analyses of nickelocene at* 101 (*upper entries*) *and at* 293 K (*lower entries*)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0	0	0	145 (3)	97 (3)	183 (3)	−34 (3)	105 (2)	−21 (3)
	0	0	0	477 (4)	366 (3)	576 (5)	−97 (5)	308 (3)	−50 (7)
C(1)	408 (4)	2626 (4)	−124 (8)	244 (15)	113 (13)	499 (22)	−62 (12)	252 (16)	−38 (14)
	334 (6)	2657 (6)	−303 (18)	795 (39)	382 (21)	1762 (76)	−94 (21)	824 (47)	−69 (33)
C(2)	526 (4)	1800 (4)	−2167 (7)	212 (15)	222 (15)	243 (15)	−41 (13)	128 (13)	41 (14)
	511 (6)	1807 (8)	−2151 (12)	745 (30)	735 (31)	822 (37)	−166 (27)	458 (30)	96 (30)
C(3)	1765 (4)	666 (4)	−771 (8)	202 (14)	192 (13)	308 (17)	−31 (13)	176 (14)	−27 (14)
	1660 (6)	756 (8)	−875 (14)	698 (31)	719 (28)	1103 (49)	−158 (26)	619 (36)	−131 (33)
C(4)	2398 (4)	788 (4)	2106 (8)	178 (14)	202 (15)	275 (17)	−59 (13)	75 (14)	35 (14)
	2239 (6)	875 (7)	1764 (14)	573 (27)	685 (31)	953 (46)	−160 (25)	223 (30)	141 (34)
C(5)	1563 (4)	1994 (4)	2519 (8)	332 (17)	247 (17)	294 (18)	−187 (15)	215 (15)	−114 (15)
	1435 (9)	2071 (10)	2263 (14)	1446 (61)	1043 (49)	946 (45)	−899 (49)	860 (47)	−568 (42)

	x	y	z	U(Å^2)		x	y	z	U (Å^2)
H(1)	−408 (51)	3500 (63)	−534 (93)	370 (129)	H(4)	3171 (61)	172 (59)	3406 (112)	393 (121)
	−490	3599	−718			3169	167	3254	
H(2)	−86 (56)	1874 (69)	−4106 (116)	443 (130)	H(5)	1765 (65)	2253 (66)	4262 (119)	506 (141)
	−162	1960	−4275			1611	2458	4162	
H(3)	2018 (59)	18 (62)	−1659 (117)	434 (128)					
	2060	−63	−1824						

Positional and vibrational parameters obtained from the two analyses are given in Table 1.*

Molecular geometry

The results of the RT analysis are quite comparable to those obtained from the RT analysis of ferrocene (Seiler & Dunitz, 1979*a*). The cyclopentadienyl ring appears to be planar within 0·004 Å, but irregular (Table 2) with apparent C—C distances of 1·343–1·428 Å (average 1·381 Å, similar to ferrocene) and Ni—C of 2·144–2·181 Å (average 2·164 Å, about 0·13 Å longer than in RT ferrocene). Also, the thermal ellipsoids show a similar pattern to that obtained in the RT analysis of ferrocene (compare Fig. 2 with the corresponding figure of Seiler & Dunitz, 1979*a*).

The molecular dimensions given by the LT analysis (Table 2) are much more regular, with C—C = 1·407–1·417 Å (average 1·413 Å) and Ni—C = 2·164–2·192 Å (average 2·178 Å). On application of thermal-motion corrections, the average values are increased to 1·423 Å for C—C and 2·185 Å for Ni—C, only slightly shorter than the corresponding distances obtained by a gas-phase electron-diffraction analysis (C—C 1·430, Ni—C 2·196 Å; Hedberg & Hedberg, 1970).

Table 2. *Bond distances* (Å) *from the* 101 *and* 293 K *analyses*

All CCC angles are 108 ± 0·3°. E.s.d.'s are about 0·004 Å for Ni—C, and 0·006 Å for C—C at 101 K (0·007 and 0·01 Å, respectively, at 293 K).

	100 K	293 K
Ni—C(1)	2·164 (2·171)*	2·144
Ni—C(2)	2·171 (2·176)	2·160
Ni—C(3)	2·191 (2·195)	2·181
Ni—C(4)	2·192 (2·199)	2·174
Ni—C(5)	2·174 (2·183)	2·161
C(1)—C(2)	1·414 (1·424)	1·375
C(2)—C(3)	1·417 (1·427)	1·343
C(3)—C(4)	1·407 (1·418)	1·348
C(4)—C(5)	1·411 (1·421)	1·409
C(5)—C(1)	1·415 (1·426)	1·428
NiC (mean)	2·178 (2·185)	2·164
C—C (mean)	1·413 (1·423)	1·381
C—H	0·87–1·03	–
C—H (mean)	0·93	

* Values in parentheses are corrected for librational motion.

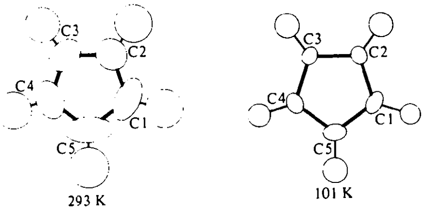

Fig. 2. Vibrational ellipsoids [50% probability level (Johnson, 1965)] of the C atoms in nickelocene at 101 and at 293 K, projected on the mean plane of a cyclopentadienyl ring.

However, the Ni—C distances seem to be unequal since their spread (0·028 Å) is greater than that of the C—C distances (0·010 Å), although the former have lower e.s.d.'s (0·003–0·005 Å against 0·005–0·007 Å). The differences among the Ni—C distances are not due to non-planarity of the cyclopentadienyl ring (planar within 0·003 Å) but rather to the fact that the Ni atom is displaced by 0·030 Å from the mean fivefold axis of the ring. In other words, although the two rings are perfectly parallel, there is a shear of 0·060 Å between the ring centres (the line joining the ring centres makes an angle of 0·91° with the normal to the rings; in the RT structure this angle is 1·64° and the shear between the ring centres amounts to 0·104 Å).

The H positions have calculated e.s.d.'s of about 0·05 Å and are less accurately determined than in the 100 K ferrocene analysis ($\sigma \sim 0{\cdot}02$ Å); the systematic error is also larger, the mean C—H distance being about 0·93 Å, compared with 1·00 Å in ferrocene. The observed displacements of the H atoms from the ring plane are small: 0·022, 0·048, 0·018, 0·025, 0·030 Å; all are less than the e.s.d. but there is a clear trend in that all are towards the metal atom, as in ferrocene. With a mean out-of-plane displacement of 0·028 Å and mean C—H = 0·93 Å, the C—H bonds would be bent out of the ring plane by 1·7°. From electron diffraction this angle was estimated by Ronova, Bochvar, Chistjakov, Struchkov & Alekseev (1969) to be about 5°, but Hedberg & Hedberg (1970) could not detect any significant deviation from planarity. The evidence for non-planarity of the rings is admittedly slight and a neutron-diffraction analysis seems necessary to settle this point.

Thermal-motion analysis

The vibrational parameters obtained in the LT analysis are generally larger than those obtained in the 100 K ferrocene analysis (Seiler & Dunitz, 1979*b*). They correspond roughly to the vibrational parameters that would be expected for ferrocene at a temperature of about 135 K, but they have larger e.s.d.'s (even larger than the ferrocene 148 K results). This loss of precision makes it impossible to draw such detailed conclusions as those reached in the ferrocene analyses.

For example, the rigid-body test (Rosenfield, Trueblood & Dunitz, 1978) is not nearly as informative as it was in the 100 K ferrocene analysis because the

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* Lists of structure factors measured at 101 and 293 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35433 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Results of rigid-body-motion analysis*

Because of the approximate D_{5d} molecular symmetry, two eigenvalues of the inertial tensor are nearly equal and the corresponding eigenvectors are very sensitive to small changes in the atomic positions. The inertial coordinate system is therefore not suitable for comparing results at different temperatures. In its place we refer all vectors to a set of Cartesian axes along **a**, **b**, **a*** × **b***. R' is $[\sum(\Delta U)^2/\sum(U^2)]^{1/2}$.

	101 K				295 K			
	Eigenvalue	Eigenvector			Eigenvalue	Eigenvector		
Fivefold axis		0·7153	0·6937	0·0840		0·7113	0·7019	0·0367
L_1 (deg^2)	45·08	0·7955	0·6057	−0·0208	199·5	0·7704	0·6324	−0·0809
L_2 (deg^2)	5·50	−0·4899	0·6225	−0·6104	17·4	−0·5291	0·5634	−0·6346
L_3 (deg^2)	1·05	−0·3567	0·4957	0·7919	3·6	−0·3557	0·5317	0·7686
T_1 ($\times 10^{-4}$ Å^2)	195	−0·1834	0·3720	−0·9099	659	−0·2354	0·4720	−0·8496
T_2 ($\times 10^{-4}$ Å^2)	150	−0·9154	0·2729	0·2960	466	−0·9545	0·0522	0·2935
T_3 ($\times 10^{-4}$ Å^2)	90	0·3585	0·8872	0·2905	300	0·1829	0·8801	0·4382
$\langle \Delta U^2 \rangle^{1/2}$ (Å^2)			15 × 10^{-4}				81 × 10^{-4}	
$\langle \sigma^2(U) \rangle^{1/2}$ (Å^2)			14 × 10^{-4}				36 × 10^{-4}	
R'			0·076				0·115	

e.s.d.'s in $\Delta_{\rm C,C}$ are about 0·0022 Å^2 compared with 0·0010 Å^2 in ferrocene. Since the r.m.s. value of Δ is 0·0018 Å^2 for the ten C,C pairs in each cyclopentadienyl ring, the test is actually satisfied as well as can be expected, but it is far less convincing than in the 100 K ferrocene analysis.

Similarly, from the 100 K ferrocene results we could detect that the C-atom framework was vibrating as a whole relative to the Fe atom; in molecule (I), for example, all ten $\Delta_{\rm Fe,C}$ values were negative, with a mean of −0·0034 Å^2, a r.m.s. deviation of 0·0006 Å^2 and an e.s.d. in individual values of 0·0007 Å^2. In LT nickelocene, the five $\Delta_{\rm Ni,C}$ values are: −10(10), −25(13), −34(11), −31(12), −17(14) × 10^{-4} Å^2, with a mean of −0·0023 Å^2 and a r.m.s. deviation of 0·0009 Å^2. We see a similar trend to that found for ferrocene, but the scatter is greater, in keeping with the larger e.s.d.'s. From Hedberg & Hedberg's (1970) electron-diffraction study, the mean-square vibration amplitude along the Ni···C directions at about 385 K is 0·0071 Å^2. However, this value is not strictly comparable with ours because it is based on a model with equal Ni—C distances. As Hedberg & Hedberg pointed out, the unusually large Ni···C vibration amplitude found by them could be an indication that the Ni—C distances are actually unequal. The spread in Ni—C distance found in the present study (0·028 Å at 100 K; 0·037 Å at RT) is probably not enough to account for the electron-diffraction value, but the apparent temperature dependence suggests that crystal-packing forces favour a more symmetrical molecular structure and hence that the molecule may be more markedly asymmetric in the gas phase.

Analysis of the atomic vibrational tensors in terms of rigid-body motion (program *THMB*; Trueblood, 1978) yielded the results shown in Table 3. The agreement between observed and calculated U^{ij} values is about as good as can be expected for the 100 K data. It is much less satisfactory for the RT data, but the two sets of results agree reasonably well, the LT eigenvalues being consistently 23–32% of the RT values with their eigenvectors pointing in approximately the same directions. We shall concentrate mainly on the LT results.

The principal libration axis L_1 lies within 10° of the molecular fivefold axis and its eigenvalue of 45·1 deg^2 is larger than the corresponding value in ferrocene (28 deg^2) at the same temperature. The effective force constant k for the motion about L_1 can be estimated from $\langle \varphi \rangle^2 = RT/k$ to be 19 J mol^{-1} deg^{-2} at 101 K, compared with 29 J mol^{-1} deg^{-2} for ferrocene at the same temperature. Of the remaining eigenvalues, L_2, T_2 and T_3 are approximately the same as in ferrocene, T_1 is larger and L_3 is smaller. Corrections for thermal motion have been applied to the interatomic distances shown in Table 2.

Crystal packing

A stereopicture of the unit cell, viewed along a direction nearly perpendicular to the *ab* plane, is shown in Fig. 3. Intermolecular H···H distances <2·8 Å are listed in Table 4 for idealized H positions (symmetrically disposed in the ring plane with C—H = 1·08 Å; the corresponding distances calculated from observed positions are 0·1–0·2 Å longer). For comparison, the corresponding distances based on the 173 K ferrocene coordinates (Seiler & Dunitz, 1979*a*) are also listed. In contrast to the LT triclinic ferrocene structure, there are no H···H distances <2·4 Å. Each molecule is in contact with 14 neighbouring molecules and makes 22 contacts <2·8 Å. The packing at 101 K is not only less tight than that of triclinic ferrocene at the same temperature (compare Table 10 of Seiler & Dunitz, 1979*b*) but also less tight than that of monoclinic ferrocene at 173 K.

One striking feature is that the shortest H···H distance, across the inversion centre at (0,$\frac{1}{2}$,0), remains

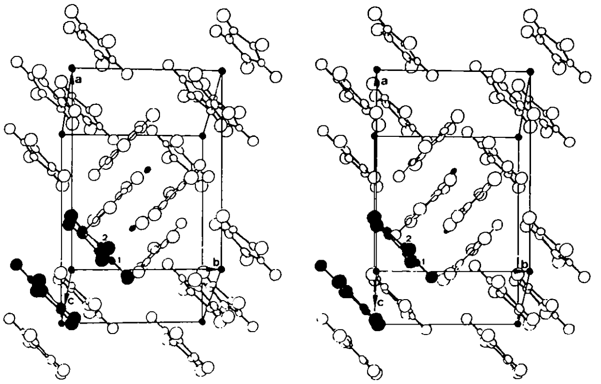

Fig. 3. Stereoscopic view of the packing in the monoclinic unit cell. The standard molecule, whose coordinates are listed in Table 1, is shaded.

Table 4. *Intermolecular* H···H *distances* (Å) *calculated from idealized positions at* 101 K *and at RT for nickelocene and at* 173 K *for ferrocene*

Distances calculated from observed positions are 0·1–0·2 Å longer. The first atom is in the asymmetric unit (x, y, z), the second in a symmetry-related unit [S indicates a molecule related by 2_1 ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $-z$), and a prime indicates an atom derived from the unit at $-x, -y, -z$].

	101 K	RT	Ferrocene (173 K)
$H(1)\cdots H(1')010$	2·42	2·40	2·40
$H(1)\cdots H(3'S)\bar{1}00$	2·56	2·62	2·51
$H(2)\cdots H(5)00\bar{1}$	2·48	2·54	2·43
$H(2)\cdots H(3')00\bar{1}$	2·51	2·61	2·41
$H(2)\cdots H(4'S)\bar{1}0\bar{1}$	2·67	2·78	2·79
$H(3)\cdots H(2')00\bar{1}$	2·51	2·61	2·41
$H(3)\cdots H(1'S)000$	2·56	2·62	2·51
$H(4)\cdots H(5S)0\bar{1}1$	2·44	2·56	2·39
$H(4)\cdots H(2'S)001$	2·67	2·78	2·79
$H(5)\cdots H(4S)001$	2·44	2·56	2·39
$H(5)\cdots H(2)001$	2·48	2·54	2·43

Idealized H positions ($\times 10^4$; C—H direction along bisector of CCC angle, C—H distance = 1·08 Å) at 101 K

	x	y	z
H(1)	−425	3571	−525
H(2)	−201	2001	−4398
H(3)	2160	−160	−1741
H(4)	3362	78	3727
H(5)	1767	2374	4505

practically constant at around 2·4 Å. Since the vector runs nearly parallel to b, a contraction along b would lead to a still shorter H(1)···H(1′) distance. This may be one of the factors responsible for the anomalous negative coefficient of expansion along the b direction.

Discussion

The monoclinic RT structures of nickelocene and ferrocene are remarkably similar, but at 100 K the two compounds have quite different crystal structures. Ferrocene has long transformed to a triclinic structure containing nearly eclipsed molecules with no crystallographic symmetry, while nickelocene retains the monoclinic RT structure with centrosymmetric staggered molecules. Of course, the molecular centre of symmetry formally required by the monoclinic crystal may be only statistical in nature. This is probably the case for ferrocene where evidence for static disorder involving different orientations of nearly eclipsed molecules has been obtained from X-ray and neutron diffraction at RT and 173 K (Seiler & Dunitz, 1979*a*; Takusagawa & Koetzle, 1979).

What about the molecular inversion centre in RT nickelocene? Is it a genuine symmetry element or is it merely statistical in nature? The marked similarity between the thermal-ellipsoid patterns of RT ferrocene and nickelocene might suggest that the degree and nature of disorder in the two crystals are also very similar. Without the LT results for nickelocene, one might well jump to the conclusion that the majority of molecules in RT nickelocene are eclipsed or nearly so, and that the structure is statically disordered, as in RT ferrocene. However, it is clear that the analogy with ferrocene cannot be pressed too far for it suggests that the two crystals should behave similarly on cooling, which is not the case. There is nothing in the behaviour of nickelocene to match the phase transition in ferrocene around 164 K. Indeed, no phase change is detectable on cooling to 5 K (Calvarin & Weigel, 1976; Rabinovich *et al.*, 1978).

Furthermore, monoclinic nickelocene at 100 K shows no obvious indications of appreciable static disorder; the molecular geometry is very regular; the vibrational parameters are somewhat larger than in triclinic ferrocene at the same temperature but by no means abnormally large. Thus, although individual molecules show dynamic disorder (the mean-square libration amplitude about L_1 is 6·7°), there is no reason to believe that they are randomly disordered over two eclipsed arrangements (related by inversion), as in monoclinic ferrocene.

Also in contrast to ferrocene, which is eclipsed in the gas phase with a barrier of 3·8 ± 1·3 kJ mol^{-1} to internal rotation (Haaland & Nilsson, 1968), the equilibrium molecular structure of nickelocene in the gas phase is by no means settled. Although Ronova *et al.* (1969) claimed that the radial distribution curve is in better accord with an eclipsed model than with a staggered one, their evidence for this is not especially convincing. Hedberg & Hedberg (1970) noted that the inter-ring distances which reflect relative ring conformation were smeared out by molecular vibration to such an extent that eclipsed and staggered models yielded equally good agreement with observation. They concluded that the rings are rotating much more freely than in ferrocene. It would thus appear that whatever the equilibrium conformation of the free nickelocene molecule may be, the barrier between eclipsed and staggered conformations is very small. The conformation in the crystal would then be determined almost exclusively by packing forces and these, in the monoclinic crystal structure, clearly favour the centrosymmetric staggered conformation.

Thus, of the two extreme models for the RT crystal, one involving dynamic disorder of centrosymmetric molecules, the other involving static disorder of non-centrosymmetric molecules, the balance of the evidence seems to suggest that the former model is closer to the mark. In order to settle the question, more information about the temperature dependence of the thermal ellipsoids would be required.

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The Structures of Bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II) and Bis(2-methoxy-4-nitrophenolato)bis(γ-picoline)copper(II)

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Abstract

Bis(pyridine)bis(2,4,6-trichlorophenolato)copper(II) is triclinic with $a = 9{\cdot}576\,(6)$, $b = 9{\cdot}017\,(7)$, $c = 9{\cdot}129\,(7)$ Å, $\alpha = 125{\cdot}61\,(8)$, $\beta = 101{\cdot}73\,(4)$, $\gamma = 94{\cdot}02\,(6)^\circ$, $Z = 1$, space group $P\bar{1}$. The structure was refined to $R = 0{\cdot}039$ for 2019 observed reflections. The compound is monomeric, the stereochemistry at Cu being the distorted, elongated, octahedral $CuN_2O_2Cl_2$ chromophore with a Cu–Cl length of 2·92 Å. Bis(2-methoxy-4-nitrophenolato)bis(γ-picoline)copper(II) is also triclinic, with $a = 10{\cdot}537\,(1)$, $b = 10{\cdot}521\,(1)$, $c = 15{\cdot}377\,(2)$ Å, $\alpha = 121{\cdot}031\,(5)$, $\beta = 110{\cdot}958\,(5)$, $\gamma = 86{\cdot}105\,(3)^\circ$, $Z = 2$, space group $P\bar{1}$. This structure was refined to $R = 0{\cdot}076$ for 3231 observed reflections. The stereochemistry at Cu is a distorted, elongated, octahedral CuN_2O_4 chromophore.

Introduction

In a series of papers entitled *Substituted Phenols as Ligands* (Bullock & Jones, 1970, 1971; Hobson, Ladd & Povey, 1973; Bullock, Hobson & Povey, 1974; Ladd & Povey, 1976) attempts were made to correlate the solid-state diffuse electronic reflectance spectra of some Cu^{II} complexes with the stereochemistry of the coordination polyhedra around the metal. Methods have been established (Hathaway & Tomlinson, 1970; Hathaway & Billing, 1970) whereby stereochemical deduc-

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