

The Structure of μ -(η -Cyclopentadienyl)-bis[(η -cyclopentadienyl)nickel(II)] Tetrafluoroborate at 190 and 295 K

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Abstract

The structure of $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ has been redetermined at 190 K. Formula weight 399.5, space group $P2_12_12_1$, $Z = 4$. Cell at 190 K: $a = 16.779$ (9), $b = 11.339$ (8), $c = 8.046$ (5) Å, $V = 1530.8$ Å³, $D_x = 1.73$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 2.50$ mm⁻¹. Cell at 295 K: $a = 17.019$ (2), $b = 11.454$ (2), $c = 8.074$ (1) Å, $V = 1573.9$ Å³, $D_x = 1.69$ Mg m⁻³, $D_o = 1.66$ (1) Mg m⁻³, $\mu(\text{Mo } K\alpha) = 2.43$ mm⁻¹. The structure was refined on F to $R = 0.039$ using 1767 data having $F_o^2 > 3\sigma(F_o^2)$ and 201 parameters. The triple-decker sandwich-type structure was confirmed. Interatomic distances are: Ni to outer ring 1.746 (12) and 1.760 (12) Å; average Ni to outer C atoms 2.090 (12) and 2.109 (20) Å; Ni to inner ring 1.791 (6) and 1.796 (6) Å; average Ni to inner C atoms 2.166 (17) and 2.162 (10) Å. The average C–C distance in the outer two rings is 1.36 (3) Å, in the inner ring 1.42 (1) Å. This difference is ascribed to higher thermal motion and/or irresolvable disorder which afflicts the outer two rings. The three C_5H_5 rings are coplanar to within 3.97°. Reduced disorder in the $[\text{BF}_4]^-$ anion and small differences in the $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ cation are observed in the 190 K determination compared to the room-temperature structure. On cooling $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ to 90 K, a reversible phase transition at 102 K is evidenced by differential-scanning-calorimetry measurements.

Introduction

Since the first simple sandwich complex, ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$, was prepared and characterized (Miller, Tebboth & Tremaine, 1952; Kealy & Pauson, 1951; Fischer & Pfab, 1952; Dunitz, Orgel & Rich, 1956) there has been curiosity in the creation, structure and properties of multiple sandwich species. The diversity of structurally characterized metal–cyclopentadienyl and related complexes is now enormous. However, triple-decker and higher species remain rare. The complex $(\text{C}_5\text{H}_5)\text{Co}(\text{cyclooctatetraene})\text{Co}(\text{C}_5\text{H}_5)$ (Paulus, Hoppe & Huber, 1967) can be considered as a

herald to the first genuine triple-decker complex, the cationic $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ moiety (Werner & Salzer, 1972; Salzer & Werner, 1972a). Since then some carborane- and thiocarborane-containing triple-decker complexes with fillings of Co and Fe respectively have been structurally characterized (Beer, Miller, Sneddon, Grimes, Mathew & Palenik, 1973; Pipal & Grimes, 1978; Siebert, Renk, Kinberger, Bochmann & Krüger, 1976). An interesting group of Fe (Maxwell, Weiss, Sinn & Grimes, 1977) and Co (for example: Grimes, Zalkin & Robinson, 1976; Callahan, Strouse, Sims & Hawthorne, 1974; Pipal & Grimes, 1979) compounds with boron and carborane cages as a type of middle layer have also been studied. Recently, the structure of a tetra-decker complex, $(\text{C}_5\text{H}_5)\text{FeLFeLFe}(\text{C}_5\text{H}_5)$, where $L = \text{SB}(\text{CH}_3)\text{C}(\text{C}_2\text{H}_5)\text{C}(\text{C}_2\text{H}_5)\text{B}(\text{CH}_3)$, was reported (Siebert, Böhle & Krüger, 1980). In view of the wider interest in these compounds (for example: Lauher, Elian, Summerville & Hoffman, 1976) and in order to interpret the stereochemistry in a broader perspective we now report in full on the structure of $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ at 190 and 295 K, the gross features of which were briefly communicated earlier (Dubler, Textor, Oswald & Salzer, 1974). The precision and accuracy of this room-temperature analysis were compromised by apparent disorder and/or high thermal motion. Thus we have undertaken a complete redetermination of the structure at 190 K.

Experimental

Preparation

The compound was prepared as described previously (Salzer & Werner, 1972a; Werner & Salzer, 1972). Crystals were grown by cooling a concentrated solution to 233 K.

Differential scanning calorimetry (DSC)

Measurements on a Perkin–Elmer DSC-2 instrument in a flowing-helium atmosphere, sample weights 5–20 mg heating/cooling rates 2.5–10 K min⁻¹. Temperature and enthalpy calibration: melting of indium (429.8 K, 28.4 J g⁻¹), melting of mercury (234.3 K) and KH_2PO_4 phase transition (122.5 K).

Crystallographic study

The orthorhombic space group $P2_12_12_1$, established by precession and Weissenberg photography at room temperature, was preserved at lower temperatures. DSC provided evidence for a phase transition at 102 K, but no endothermic or exothermic reaction was indicated in the temperature range 110 to 300 K. Nonetheless, at temperatures below 170 K, single crystals already had a disturbing tendency to explode.

Room-temperature data: Picker FACS-I diffractometer, unit-cell parameters and crystal orientation determined by the least-squares refinement of 12 automatically centered reflections in the range $0.220 < (\sin \theta)/\lambda < 0.372 \text{ \AA}^{-1}$. Three standard reflections, data appropriately scaled for the anisotropic 5% decrease of the observed intensities. Data collected up to $(\sin \theta)/\lambda = 0.54 \text{ \AA}^{-1}$, 1036 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. Data processed and corrected for Lorentz, polarization and absorption effects using the XRAY 72 program package (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).^{*} Atomic scattering factors of Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965); anomalous-dispersion correction for Ni (Cromer & Liberman, 1970). Very high thermal motion and/or disorder afflicted the cyclopentadienyl rings; disorder in the $[\text{BF}_4]^-$ anion could be resolved. An alternative description of the disorder of the two outer C_5H_5 rings assumed rotational disorder of the rings about the $\text{Ni}\cdots\text{Ni}$ axis, leading to a pseudo-toroidal electron density distribution, which was modelled by three positions for each C atom, each with an occupancy of 0.333. This did not lead to a better refinement of the structure. Final R values are $R = 0.063$ and $R_w = 0.068$ including all observed reflections. Atomic parameters for the room-temperature structure are given in Table 1.

190 K data: the intensities were significantly enhanced and background radiation was lowered. Crystal orientation and unit-cell parameters determined by hand-centering 12 reflections in the range $0.359 < (\sin \theta)/\lambda < 0.457 \text{ \AA}^{-1}$ using $\text{Mo } K\alpha_1$ ($\lambda = 0.7093 \text{ \AA}$) radiation. Data collected up to $(\sin \theta)/\lambda = 0.705 \text{ \AA}^{-1}$, 1767 unique reflections with $F_o^2 > 3\sigma(F_o^2)$. Modified Nonius low-temperature unit. Structure completely redetermined for the low-temperature data set. Disorder of the $[\text{BF}_4]^-$ group is no longer evident and the apparent thermal motions of the cyclopentadienyl rings and the Ni atoms are generally smaller. An adequate weighting scheme was chosen in which the function minimized $[\sum w(|F_o| - |F_c|)^2]$ was independent of the magnitude of F_o and $(\sin \theta)/\lambda$; an absorption

Table 1. Final atomic parameters with e.s.d.'s for $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ at 295 K (first line) and at 190 K (second line)

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

	x	y	z	B_{eq} (\AA^2)
Ni(1)	0.1654 (1)	-0.3090 (2)	0.3447 (3)	5.1
	0.16493 (5)	-0.30547 (6)	0.33305 (9)	3.3
Ni(2)	0.0857 (2)	-0.1213 (2)	0.6562 (3)	5.8
	0.08933 (5)	-0.11167 (7)	0.64830 (10)	3.6
C(11)	0.144 (2)	-0.456 (2)	0.196 (3)	9.0
	0.1437 (6)	-0.4556 (8)	0.1853 (13)	6.8
C(12)	0.162 (2)	-0.358 (2)	0.098 (3)	10.4
	0.1616 (9)	-0.3577 (9)	0.0847 (10)	8.5
C(13)	0.242 (2)	-0.329 (2)	0.141 (4)	13.4
	0.2342 (10)	-0.3230 (10)	0.1210 (20)	10.6
C(14)	0.260 (2)	-0.412 (4)	0.268 (5)	15.5
	0.2650 (8)	-0.3910 (18)	0.2374 (25)	14.2
C(15)	0.202 (2)	-0.478 (3)	0.285 (4)	11.2
	0.2098 (10)	-0.4737 (9)	0.2788 (13)	9.4
C(21)	0.151 (1)	-0.134 (2)	0.427 (3)	6.9
	0.1521 (4)	-0.1254 (5)	0.4163 (8)	3.8
C(22)	0.188 (1)	-0.204 (2)	0.554 (3)	9.0
	0.1931 (4)	-0.1929 (7)	0.5386 (9)	4.9
C(23)	0.133 (1)	-0.293 (2)	0.602 (2)	7.3
	0.1411 (5)	-0.2832 (6)	0.5955 (8)	4.6
C(24)	0.070 (1)	-0.280 (2)	0.513 (3)	6.9
	0.0684 (4)	-0.2728 (5)	0.5088 (8)	3.9
C(25)	0.077 (1)	-0.183 (2)	0.405 (3)	6.6
	0.0742 (3)	-0.1753 (5)	0.3977 (7)	3.3
C(31)	0.505 (3)	-0.409 (3)	0.160 (5)	14.2
	0.5219 (12)	-0.4155 (9)	0.1358 (17)	12.2
C(32)	0.481 (2)	-0.468 (4)	0.280 (5)	13.0
	0.4917 (6)	-0.4782 (11)	0.2592 (18)	9.3
C(33)	0.459 (2)	-0.047 (2)	0.183 (4)	10.7
	0.4553 (7)	-0.0616 (7)	0.1861 (10)	6.4
C(34)	0.106 (2)	0.028 (3)	0.801 (5)	13.8
	0.1113 (6)	0.0473 (8)	0.7815 (13)	7.1
C(35)	0.079 (3)	-0.072 (3)	0.901 (3)	14.5
	0.0982 (11)	-0.0429 (11)	0.8915 (12)	11.0
B	0.3859 (9)	-0.1819 (16)	0.7633 (21)	4.5
	0.3913 (4)	-0.1873 (7)	0.7661 (10)	3.9
F(1)*	0.4167 (9)	-0.2548 (9)	0.8806 (15)	13.0
	0.4230 (4)	-0.2677 (4)	0.8766 (6)	7.7
F(2)*	0.3215 (5)	-0.1402 (11)	0.8263 (15)	9.9
	0.3189 (2)	-0.1483 (4)	0.8246 (6)	5.7
F(3)	0.3783 (5)	-0.2442 (7)	0.6310 (10)	9.6
	0.3819 (2)	-0.2443 (4)	0.6150 (5)	5.3
F(4)*	0.4395 (6)	-0.0959 (9)	0.7571 (14)	9.4
	0.4433 (3)	-0.0935 (4)	0.7506 (6)	6.1
F(5)†	0.344 (3)	0.087 (3)	0.731 (6)	7.7
F(6)†	0.449 (3)	0.178 (4)	0.816 (5)	7.1
F(7)†	0.336 (4)	0.227 (5)	0.882 (5)	9.4

* Occupancy fixed at 0.85 (295 K), 1.00 (190 K).

† Occupancy fixed at 0.15 (295 K).

correction using analytical integration was applied. H atoms were included at their calculated idealized positions as a fixed contribution to F_c . The correct enantiomorph was established by parallel refinements (x, y, z versus x, y, z); it was found to be the opposite of that initially assumed ($R = 0.039$, $R_w = 0.047$ versus $R = 0.043$, $R_w = 0.051$). Final atomic parameters for the 190 K structure are given in Table 1.*

* Details of crystal and data-collection parameters, anisotropic thermal parameters, hydrogen-atom parameters, non-bonding intermolecular $\text{C}\cdots\text{F}$ contact distances, least-squares planes for the cp rings and lists of structure factors obtained at 295 and 190 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38141 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* The XRAY program package was used as implemented on the CDC computer of the ETH, Zürich; final refinements of the 190 K structure were performed on the University of Zürich IBM 3033 computer using a local version of the Northwestern University crystallographic computing library (for example, see Waters & Ibers, 1977).

Description and discussion of the structure

General

The cation $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ is illustrated in Fig. 1, along with the atom-labeling scheme. Bond distances and angles describing the geometry are given in Tables 2 and 3. Because of greater precision and insignificant differences in bond distances and angles only the low-temperature results are tabulated. The crystal structure, illustrated in Fig. 2, comprises discrete units of $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ cations and $[\text{BF}_4]^-$ anions. The $[\text{BF}_4]^-$ group is important in determining crystal packing, since there are an unusually large number of $\text{F}\cdots\text{C}$ van der Waals contacts in the range 3.14 to 3.50 Å. Furthermore, while rings cp(1) and cp(2) are nearly coplanar (making an angle of 1.26°), ring cp(3) is tilted by 3.45° [cp(1)] and 3.97° [cp(2)] from coplanarity with the other two rings; this is presumably a consequence of the unusual crystal packing. All three cp rings are planar to within 0.003 Å. The relative orientation of the three rings [cp(1) and cp(2) are approximately eclipsed, while cp(3) is staggered with respect to the other two] may also be attributed to crystal packing forces and not to some electronic factors intrinsic to an $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ cation.

With two Ni atoms competing for electron density it is unsurprising that the Ni–C separations for atoms belonging to ring cp(2) are somewhat longer than the Ni–C separations to the outer two rings. This is consistent with the fact that in substitution reactions on the $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ cation with Lewis bases, a preferential cleavage of the Ni–inner-ring bonds is observed (Salzer & Werner, 1972*b*). The cp rings are quite comfortably disposed at van der Waals separations with respect to one another. While the longer C–C bond lengths in the doubly coordinated ring cp(2)

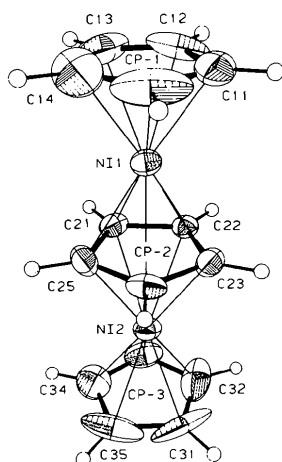


Fig. 1. ORTEP diagram (Johnson, 1965) of the $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ cation at 190 K. Thermal ellipsoids are drawn at the 30% probability level. H atoms are given artificially small thermal parameters.

[compared to the singly coordinated outer rings cp(1) and cp(3)] are in accord with most notions of chemical reasonableness, regrettably the difference is not significant since the C–C bonds in the outer two rings are

Table 2. Bond distances (Å) for $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ at 190 K

Ni(1)–C(11)	2.107 (7)	Ni(2)–C(31)	2.096 (9)
Ni(1)–C(12)	2.085 (7)	Ni(2)–C(32)	2.082 (9)
Ni(1)–C(13)	2.074 (10)	Ni(2)–C(33)	2.124 (7)
Ni(1)–C(14)	2.086 (10)	Ni(2)–C(34)	2.129 (8)
Ni(1)–C(15)	2.096 (8)	Ni(2)–C(35)	2.112 (8)
Average	2.090 (12)	Average	2.109 (20)
Ni(1)–C(21)	2.159 (6)	Ni(2)–C(21)	2.150 (6)
Ni(1)–C(22)	2.142 (6)	Ni(2)–C(22)	2.159 (7)
Ni(1)–C(23)	2.164 (7)	Ni(2)–C(23)	2.172 (7)
Ni(1)–C(24)	2.181 (6)	Ni(2)–C(24)	2.173 (7)
Ni(1)–C(25)	2.183 (6)	Ni(2)–C(25)	2.157 (6)
Average	2.166 (17)	Average	2.162 (10)
C(11)–C(12)	1.41 (1)	C(31)–C(32)	1.33 (2)
C(11)–C(15)	1.36 (1)	C(31)–C(35)	1.38 (2)
C(12)–C(13)	1.31 (2)	C(32)–C(33)	1.38 (1)
C(13)–C(14)	1.32 (2)	C(33)–C(34)	1.37 (1)
C(14)–C(15)	1.36 (2)	C(34)–C(35)	1.37 (1)
Average	1.35 (4)	Average	1.37 (2)
C(21)–C(22)	1.424 (9)	B–F(1)	1.377 (8)
C(21)–C(25)	1.433 (9)	B–F(2)	1.386 (9)
C(22)–C(23)	1.421 (10)	B–F(3)	1.380 (9)
C(23)–C(24)	1.410 (9)	B–F(4)	1.380 (8)
C(24)–C(25)	1.425 (8)	Average	1.381 (4)
Average	1.423 (8)		
Metal–ring distances			
Ni(1)–cp(1)	1.746 (12)	Ni(2)–cp(2)	1.791 (6)
Ni(1)–cp(2)	1.796 (6)	Ni(2)–cp(3)	1.760 (12)

Table 3. Bond angles ($^\circ$) for $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ at 190 K

C(15)–C(11)–C(12)	105.3 (9)	C(35)–C(31)–C(32)	107.6 (10)
C(11)–C(12)–C(13)	107.9 (10)	C(31)–C(32)–C(33)	110.2 (12)
C(12)–C(13)–C(14)	110.2 (13)	C(32)–C(33)–C(34)	106.1 (9)
C(13)–C(14)–C(15)	108.1 (12)	C(33)–C(34)–C(35)	108.7 (10)
C(14)–C(15)–C(11)	108.5 (11)	C(34)–C(35)–C(31)	107.5 (12)
C(25)–C(21)–C(22)	107.5 (5)	F(1)–B–F(2)	110.4 (6)
C(21)–C(22)–C(23)	108.2 (6)	F(1)–B–F(3)	109.9 (6)
C(22)–C(23)–C(24)	108.1 (6)	F(1)–B–F(4)	109.4 (6)
C(23)–C(24)–C(25)	108.5 (6)	F(2)–B–F(3)	110.6 (6)
C(24)–C(25)–C(21)	107.6 (5)	F(2)–B–F(4)	107.5 (6)
		F(3)–B–F(4)	108.9 (6)

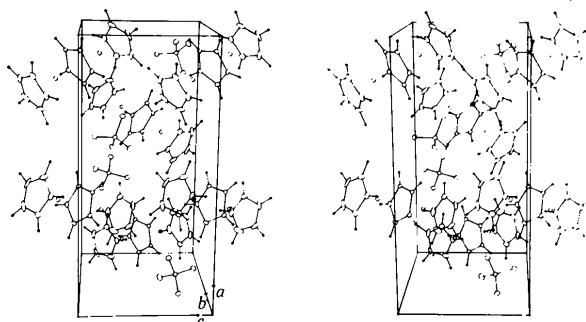


Fig. 2. The packing of $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ cations and $[\text{BF}_4]^-$ anions in the unit cell at 190 K.

severely foreshortened by the high thermal motion and/or irresolvable disorder that is readily apparent in Fig. 1. However, the mean C—C distances in the inner ring are insignificantly different from those observed in other cyclopentadienyl species (see Table 4); a lengthening of these C—C bonds due to the η^5 coordination to two Ni atoms as opposed to one in simple sandwich compounds is not apparent.

Comparison of the two structures

Although the room-temperature structure of the triple-decker complex is compromised by disorder and/or high thermal motion a number of qualitative points can be usefully made. First, the apparent thermal motions of ring cp(2), the Ni atoms and the $[\text{BF}_4]^-$ group are decreased on cooling while those of rings cp(1) and cp(3) remain essentially unperturbed (see Fig. 3). Further, it might be expected that in a given ring each atom would have similar r.m.s. components of thermal displacement if the apparent irresolvable disorder involved merely hindered rotation about the Ni...Ni axis. Such does not appear to be the case here and indeed the non-uniformity of these components and also the C—C separations which are apparent in the

low-temperature structure are paralleled to a considerable extent in the less precise room-temperature structure. Thus, complex disorder seems probable. The recent highly detailed X-ray studies by Seiler & Dunitz (1979*a*, 1979*b*, 1980) and by Clec'h, Calvarin, Bérar & Kahn (1978) on ferrocene and nickelocene and neutron diffraction studies by Takasugawa & Koetzle (1979) on ferrocene at various temperatures are pertinent to the above discussion.

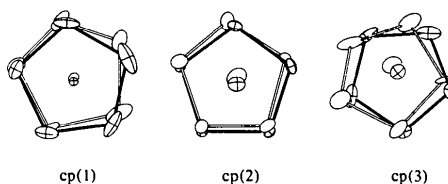


Fig. 3. Comparison of the relative orientations of the cyclopentadienyl rings of the $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ cation at 190 K (shaded) and 295 K (unshaded). The orientation-defining vectors are the same for each ring, namely the Ni...Ni vector and a vector in the plane of ring cp(1) at 190 K. The viewing origin is at the midpoint of the Ni...Ni vector. Differences which may be attributed to transferring the fractional coordinates of the structure at 295 K into the unit cell at 190 K are small (at most $\sim 1.4\%$).

Table 4. Stereochemistry of selected cyclopentadienyl 3d-metal sandwich complexes (distances in Å)

Compound	M -ring ^(a)	M -C ^(b)	C—C	VE ^(c)	Technique*
$\text{V}^{\text{II}}(\text{C}_5\text{H}_5)_2$	1.928 (6)	2.280 (5)	1.434 (3)	15	ED ⁽¹⁾
$\text{Cr}^{\text{II}}(\text{C}_5\text{H}_5)_2$	1.798 (4)	2.169 (4)	1.431 (2)	16	ED ⁽¹⁾
$\text{Mn}^{\text{II}}(\text{C}_5\text{H}_5)_2$	2.050	2.383 (3)	1.429 (5)	17 (high-spin)	ED ⁽²⁾
$\text{Mn}^{\text{II}}[\text{C}_5(\text{CH}_3)_5]_2$	1.734	2.112 (3)	1.418 (4)	17 (low-spin)	X-ray ⁽³⁾
$\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5)_2$	1.661	2.064 (3)	1.440 (2)	18	ED ⁽⁴⁾
	1.648	2.046 (3)	1.426 (3)		X-ray ⁽⁵⁾
	(1.651) ^(d)	(2.052)	(1.433)		(101 K)
$\text{Co}^{\text{II}}(\text{C}_5\text{H}_5)_2$	1.739 (2)	2.119 (3)	1.429 (2)	19	ED ⁽⁶⁾
	1.725	2.096 (8)	1.41 (1)		X-ray ⁽⁷⁾
					(100 K)
$\text{Ni}^{\text{II}}(\text{C}_5\text{H}_5)_2$	1.828	2.196 (4)	1.430 (2)	20	ED ⁽⁸⁾
	1.816	2.178 (13)	1.413 (6)		X-ray ⁽⁹⁾
	(1.819) ^(d)	(2.185)	(1.423)		
$\text{Ni}^0(\text{C}_5\text{H}_5)[\text{C}_3(\text{C}_6\text{H}_5)_3]$	1.726 (C_5H_5)	2.100 (6)	1.405 (9)		X-ray ⁽¹⁰⁾
	1.779 (C_3)	—	—		
$\text{Ni}^{\text{II}}(\text{C}_5\text{H}_5)[\text{C}_3\text{B}_2(\text{C}_2\text{H}_5)_4(\text{CH}_3)]$	1.715 (C_5H_5)	2.076 (12)	1.37 (3)		X-ray ⁽¹¹⁾
	1.656 (C_3B_2)	—	—		
Triple-decker complexes					
$[(\text{C}_5\text{H}_5)\text{Ni}^{\text{II}}(\text{C}_5\text{H}_5)\text{Ni}^{\text{II}}(\text{C}_5\text{H}_5)]^+$	1.753 (outer)	2.098 (18)	1.36 (3)	34	X-ray ⁽¹²⁾
	1.794 (inner)	2.164 (13)	1.423 (8)		(190 K)
$[(\text{C}_5\text{H}_5)\text{Co}^{\text{III}}(\text{C}_2\text{B}_3\text{H}_4(\text{CH}_3))\text{Co}^{\text{III}}(\text{C}_5\text{H}_5)]^0$	1.570 (inner)	—	—	30	X-ray ⁽¹³⁾
$[(\text{C}_5\text{H}_5)\text{Co}^{\text{III}}(\text{C}_3\text{B}_3\text{H}_7)\text{Co}^{\text{III}}(\text{C}_5\text{H}_5)]^0$	1.660 (1) (C_5H_5)	2.041 (23)	1.394 (6)	30	X-ray ⁽¹⁴⁾
	1.568 (1) ($\text{C}_3\text{B}_3\text{H}_7$)	—	—		
$[(\text{C}_5\text{H}_5)\text{Fe}^{\text{II}}(\text{C}_2\text{B}_2\text{S}(\text{C}_2\text{H}_5)_2(\text{CH}_3)_2)\text{Fe}^{\text{II}}(\text{C}_5\text{H}_5)]^0$	1.618 ($\text{C}_2\text{B}_2\text{S}$)	—	—	30	X-ray ⁽¹⁵⁾
Tetra-decker complex					
$[(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_2\text{B}_2\text{S}(\text{C}_2\text{H}_5)_2(\text{CH}_3)_2)_2\text{Fe}]$	1.67 (C_5H_5)	—	—	42	X-ray ⁽¹⁶⁾
	1.635 ($\text{C}_2\text{B}_2\text{S}$)	—	—		

Notes: (a) M -ring is the perpendicular displacement of the metal atom from the plane of the ring. Average values are given where the distances are not forced by symmetry to be equal. (b) The e.s.d. given in parentheses is the larger of that for an individual parameter as calculated from the inverse to the least-squares matrix or that for the scatter of parameters about their mean. (c) VE: valence electrons [for details see Siebert *et al.* (1976)]. (d) Parameters adjusted for the effects of thermal motion are given in parentheses.

* References (ED: electron diffraction): (1) Gard, Haaland, Novak & Seip (1975); (2) Almennigen, Haaland & Motzfeldt (1967); (3) Freyberg, Robbins, Raymond & Smart (1979); (4) Haaland & Nilsson (1968); (5) Seiler & Dunitz (1979*a,b*); (6) Almennigen, Gard & Haaland (1976); (7) Bünder & Weiss (1975); (8) Hedberg & Hedberg (1970); (9) Seiler & Dunitz (1980); (10) Tuggle & Weaver (1971); (11) Siebert, Bochmann, Edwin, Krüger & Tsay (1978); (12) this paper; (13) Beer *et al.* (1973); (14) Pipal & Grimes (1978); (15) Siebert, Renk, Kinberger, Bochmann & Krüger (1976); (16) Siebert, Böhle & Krüger (1980).

On cooling, any kind of discontinuous phase transition, such as ordering of $[\text{BF}_4]^-$ groups or reorientation of cyclopentadienyl rings should give rise to an exothermic peak in a DSC curve. Since no peak is registered when cooling $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ from room temperature to 190 K, it is concluded that the ordering of the $[\text{BF}_4]^-$ anions, evidenced by the crystal structure determinations at both temperatures, is a slow, continuous process over a wide temperature range and therefore not detectable by DSC. On cooling $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ to 90 K, a completely reversible phase transition at about 102 K (Fig. 4) with an approximate transition enthalpy of 0.12 kJ mol^{-1} was detected. If it is kept in mind that the complex disorder in at least two of the three cyclopentadienyl rings is still present at 190 K, this phase transition may be interpreted as an order/disorder transition involving the arrangement of the cyclopentadienyl rings. No significant hysteresis of the phase-transition temperature occurred in heating/cooling cycles of the DSC experiments. The corresponding entropy of transition estimated by $\Delta S = \Delta H/T$ is about $1.2 \text{ J K}^{-1} \text{ mol}^{-1}$.

This transition entropy in $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ is surprisingly low compared to the value of $5.3 \text{ J K}^{-1} \text{ mol}^{-1}$ (Edwards, Kington & Mason, 1960; Edwards & Kington, 1962) or $5.5 \text{ J K}^{-1} \text{ mol}^{-1}$ (Ogasahara, Sorai & Suga, 1979) measured by adiabatic calorimetry for a similar phase transition in ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$ at about 164 K, which is also attributed to reordering of C_5H_5 rings. Our DSC measurements of the ferrocene transition at 164 K (which is connected with a very small, but significant, second transition at about 170 K), however, resulted in substantially lower transition entropies of about $1.7 \text{ J K}^{-1} \text{ mol}^{-1}$. Preliminary DSC investigations of deuterated ferrocene samples showed that the transition at 164 K still occurs at exactly the same temperature with a slight decrease (about 20%) of the transition enthalpy and hence its entropy, whereas the second transition temperature shifts from 170 to about 172 K. In general, the lower entropy for the ferrocene transition found in our DSC experiments compared to adiabatic calorimetry data reported in the

literature may partly be due to the different type of measuring conditions (DSC: typical heating rates of $1\text{--}10 \text{ K min}^{-1}$ and sample weights of $1\text{--}20 \text{ mg}$. Adiabatic calorimetry: stepwise heating with very low overall heating rates and sample weights of $5\text{--}100 \text{ g}$). In addition, the transition entropies measured for ferrocene may be dependent on the thermal history of the samples investigated, since the 164 K transition is claimed to be a transition between metastable phases (Ogasahara, Sorai & Suga, 1979), whereas the transition between the thermodynamically stable phases should occur at 242 K with an entropy of transition of $17.1 \text{ J K}^{-1} \text{ mol}^{-1}$.

Relevant structural parameters of a number of related complexes are summarized in Table 4. The correlation of M -ring separations for $M^{II}(\text{C}_5\text{H}_5)_2$ species with effective atomic number is well documented, with minimum M -ring separation occurring for $\text{Fe}(\text{C}_5\text{H}_5)_2$ and maxima at either end of the transition-metal series. Somewhat surprisingly, the average Ni-ring separation of 1.773 \AA for $[\text{Ni}_2(\text{C}_5\text{H}_5)_3]^+$ is apparently shorter than the average Ni-ring separation of 1.816 \AA for $\text{Ni}(\text{C}_5\text{H}_5)_2$.

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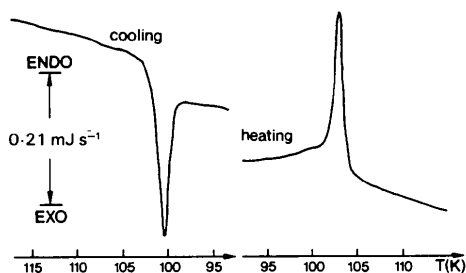


Fig. 4. DSC curves for $[\text{Ni}_2(\text{C}_5\text{H}_5)_3][\text{BF}_4]$ showing a reversible phase transition occurring at about 102 K. The corresponding transition enthalpy is 0.12 kJ mol^{-1} . (Perkin-Elmer DSC-2, heating/cooling rate 5 K min^{-1} , helium atmosphere.)

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Magnetic Properties and X-ray Crystal Structure of Tris(4-morpholinecarbodithioato)iron(III)–Dichloromethane at 20, 110, 178 and 293 K*

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Abstract

The crystal structure of $\text{Fe}(\text{S}_2\text{CNC}_4\text{H}_8\text{O})_3 \cdot \text{CH}_2\text{Cl}_2$, $M_r = 627.51$, has been determined from X-ray four-circle single-crystal diffractometer data at 20 (2), 110 (2), 178 (2) and 293 (1) K. Refinements converged to R values of 0.055, 0.062, 0.061 and 0.041 for 1320, 2720, 2048 and 1601 reflexions, respectively. The crystal structure shows a phase transition at ~ 150 K, both phases being triclinic with space group $P\bar{1}$ and $Z = 2$. The complexes are mononuclear with pseudosymmetry D_3 and are van der Waals packed. The dichloromethane molecules are located close to the FeS_6 core of the complexes and show some evidence of hydrogen bonding to S. The magnetic properties were investigated with the Faraday method and μ_{eff} varies between 3.80 (2) at 20 K and 5.60 (6) BM at 293 K ($1 \text{ BM} = 9.274 \times 10^{-24} \text{ J T}^{-1}$). The geometry of the FeS_6 core shows the same correlation to μ_{eff} as do other tris(dithiocarbamato)iron(III) structures. The intermediate μ_{eff} at low temperatures is explained by a

change in crystal packing and hydrogen bonding at the phase transition. Earlier explanations (a spin quartet ground state, strong hydrogen-bond interaction, cooperative effects, and desolvation) are invalidated.

Introduction

The magnetic behaviour of most substituted tris(dithiocarbamato)iron(III) $[\text{Fe}(\text{dtc})_3]$ compounds can be described as a thermal equilibrium between the low-spin doublet and the high-spin sextet states of iron(III). The effective magnetic moment, μ_{eff} , is thus expected to vary between ~ 2 BM ($1 \text{ BM} = 9.274 \times 10^{-24} \text{ J T}^{-1}$) (the low-temperature limit) and 5.92 BM (the high-temperature limit). In the case of tris(4-morpholinecarbodithioato)iron(III)–dichloromethane the μ_{eff} vs T curve is intermediate between that for a pure high-spin compound and that with a complete high-spin to low-spin transition (Fig. 1a). This anomalous behaviour has been subject to numerous investigations (Butcher & Sinn, 1976a,b; Butcher, Ferraro & Sinn, 1976; Rinninger, Duffy, Weir, Gelerinter, Stanford & Uhrich, 1977; Haddad, Federer, Lynch & Hen-

* Compounds with Intermediate Spin. 8. Part 7: Ståhl & Ymén (1983).