O(9)—Cl(2)—O(11)	109.0 (5)	O(10)—Cl(2)—O(11)	109.6 (5)
O(9)—Cl(2)—O(12)	112.7 (5)	O(10)—Cl(2)—O(12)	107.5 (5)
O(11)—Cl(2)—O(12)	110.1 (4)		

The ligand 4,7-diazadecanediamide was prepared from ethylenediamine (13.2 ml, 0.2 mol) and acrylamide (28.4 g, 0.4 mol) in absolute ethanol (100 ml) by heating the solution under dinitrogen gas and refluxing for 2 h. The solution was cooled and the precipitate filtered off, washed with absolute ethanol, recrystallized twice from methanol, and dried in air. Equimolar quantities of $Ni(ClO_4)_2.6H_2O$ and ligand were added to water (100 ml) and the solution allowed to react overnight at room temperature. The orange products were dried by evacuation using a rotary pump and were recrystallized twice from ethanol. The structure was solved by direct methods and refined by full-matrix least squares. *SHELXTL/PC* (Siemens, 1990) was used for all the calculations.

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Lists of structure factors, anisotropic displacement coefficients and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71049 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1039]

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Structure of μ-Pyrazine-bis[bis(hexafluoroacetylacetonato)copper(II)]

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Abstract

The title structure, μ-pyrazine-bis[bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)copper(II)], consists of a centrosymmetric dimer containing a bridging molecule of pyrazine. The pyrazine is essentially planar and coordinates axially to two symmetry-related molecules of $Cu(F_6acac)_2$, where acac is acetylacetone [Cu(1)—N(1) = 2.248 (6) Å]. The Cu atoms have square-pyramidal coordination geometries and are displaced by 0.235 (5) Å from the least-squares plane defined by the four O atoms of the basal F_6acac^- ligands.

Comment

Pyrazine is capable of forming a number of interesting complexes through coordination to one or more transtion-metal centers (Kaim, 1983). When reacted with Cu^{II}, complexes exhibiting three distinct structural motifs have been identified, these being discrete dimeric complexes containing a bridging molecule of pyrazine (Belford, Fenton & Truter, 1974; Haddad, Hendrickson, Cannady, Drago & Bieksza, 1979), infinite one-dimensional chain-type structures consisting of alternating molecules of pyrazine and Cu^{II} complex (Belford, Fenton & Truter 1974; Richardson & Hatfield, 1976; Santoro, Mighell & Reimann, 1970; Valentine, Silverstein & Soos, 1974), and two-dimensional networks consisting of sheets of Cu^{II} atoms bridged by bidentate pyrazine groups (Dariet, Haddad, Duesler & Hendrickson, 1979). The structures and magnetic properties of many of these systems have been investigated in some detail. Very weak antiferromagnetic couplings are observed in discrete molecular Cu^{II} complexes (Haddad, Hendrickson, Cannady, Drago & Bieksza, 1979). Magnetic data for Cu^{II}–pyrazine systems with chain-type structures can be described using a one-dimensional anisotropic Heisenberg model for antiferromagnetically coupled systems (Losee, Richardson & Hatfield, 1973; Richardson & Hatfield, 1976), whereas magnetic susceptibility data for the two-dimensional Cu^{II}–pyrazine complexes have adequately fitted to a theoretical equation for a two-dimensional Heisenberg antiferromagnet (Dariet, Haddad, Duesler & Hendrickson, 1979).

The reaction of bis(hexafluoroacetylacetonato)-copper(II)hydrate, $Cu(F_6acac)_2(H_2O)$, with pyrazine has been reported to yield two distinct products, depending on the reaction stoichiometry. The first of these is a centrosymmetric dimer where two $Cu(F_6acac)_2$ molecules are bridged symmetrically by a bidentate pyrazine ligand. The second product consists of a complex comprised of infinite chains of bridging pyrazine groups alternating with molecules of $Cu(F_6acac)_2$ (Belford, Fenton & Truter, 1974). Recently we repeated this reaction using pyrazine and anhydrous $Cu(F_6acac)_2$ and succeeded in isolating one of these products (I), in good yield. Although the structure does not differ significantly from that reported earlier (Belford, Fenton & Truter, 1974),

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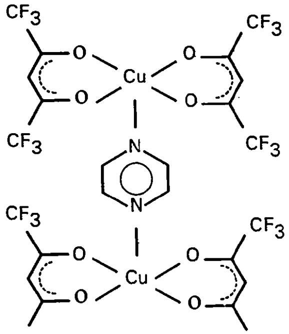
the results of our X-ray crystal structure determination proved to be of significantly greater precision.



(I)

From the results of our crystal-structure determination we find no significant differences in either the bond lengths or angles associated with Cu(1) and our values are in good agreement with those reported earlier (Belford, Fenton & Truter, 1974). Bonds to the O atoms of the F_6acac ligands average 1.951 (5) Å in length, and the distance to N(1) of the pyrazine ligand is 2.248 (6) Å. The Cu atom exhibits a square-pyramidal geometry and is displaced by 0.235 (5) Å from the least-squares plane defined by the four basal O atoms to which it is attached.

The major differences between the results of the two structure determinations involve the bridging pyrazine ligand. We find, for example, that the N—C bond lengths observed in our structure are not only nearly identical in length [N(1)—C(11) = 1.327 (11), N(1)—C(12) = 1.326 (10) Å] but also shorter by 0.05 Å on average, than those previously reported. The shortened C—N bond lengths are compensated for by an increase in the lengths of the two symmetry-equivalent C—C bonds which, in our structure, are longer and measure 1.378 (12) Å. These values agree well with, and are nearly identical to, those reported in the polymeric Cu–pyrazine complex, $[Cu(F_6acac)_2(pyrazine)]_n$ (Belford, Fenton & Truter, 1974). Despite small discrepancies in the bond lengths associated with the bridging pyrazine ligand, we note that in both structures the pyrazine group exhibits an almost perfectly planar geometry.

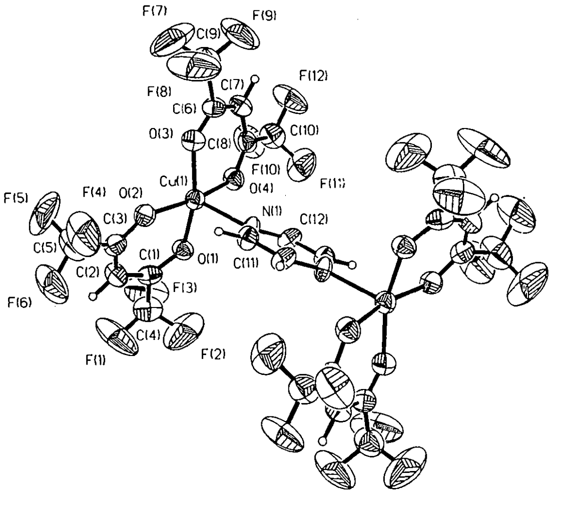


Fig. 1. A perspective view of the structure illustrating the atomic numbering scheme.

Experimental

Crystal data

$[Cu_2(C_5HF_6O_2)_4(C_4H_4N_2)]$
M_r = 1035.4
Monoclinic
$P2_1/c$
a = 10.760 (3) Å
b = 6.763 (3) Å
c = 23.722 (6) Å
β = 93.05 (2)°
V = 1723.8 (10) Å^3
Z = 2
D_x = 1.995 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 7.5–15°
μ = 1.410 mm^{-1}
T = 295 K
Prismatic habit
0.40 × 0.16 × 0.08 mm
Green
Crystal source: chloroform/pentane solution

Data collection

Siemens *R3m/V* diffractometer
ω scans
Absorption correction: none
2488 measured reflections
1630 independent reflections
1630 observed reflections
$R_{\rm int}$ = 0.0201

$\theta_{\rm max}$ = 20°
$h = 0 \rightarrow 10$
$k = -2 \rightarrow 6$
$l = -22 \rightarrow 22$
3 standard reflections monitored every 97 reflections intensity variation: <2%

Refinement

Refinement on F
Final R = 0.0745
wR = 0.0591
S = 0.96
1630 reflections
271 parameters
$w = 1/[\sigma^2(F) + 0.0013F^2]$

$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.48 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.45 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

H atoms were included in idealized riding positions with fixed isotropic U = 0.080 Å^2. Computing used *SHELXTL-Plus* (Sheldrick, 1990)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U_{\rm eq}$
Cu(1)	0.4443 (1)	0.1685 (2)	0.1171 (1)	0.039 (1)
F(1)	0.8846 (6)	−0.1466 (12)	0.1624 (4)	0.149 (4)
F(2)	0.8132 (7)	−0.1493 (12)	0.0792 (3)	0.150 (4)
F(3)	0.7394 (6)	−0.3325 (10)	0.1364 (3)	0.123 (3)
F(4)	0.6284 (7)	0.5932 (12)	0.2444 (3)	0.132 (4)
F(5)	0.6095 (8)	0.3483 (15)	0.2958 (3)	0.170 (5)
F(6)	0.7826 (6)	0.4179 (10)	0.2651 (3)	0.122 (3)

F(7)	0.0484 (7)	0.2704 (14)	0.1984 (3)	0.169 (5)
F(8)	0.1154 (6)	0.5331 (12)	0.1688 (4)	0.142 (4)
F(9)	−0.0181 (6)	0.3792 (13)	0.1217 (3)	0.143 (4)
F(10)	0.2162 (5)	−0.3761 (8)	0.0532 (3)	0.096 (3)
F(11)	0.2402 (6)	−0.2066 (10)	−0.0195 (3)	0.103 (3)
F(12)	0.0653 (5)	−0.2054 (9)	0.0188 (3)	0.104 (3)
O(1)	0.5896 (5)	−0.0043 (8)	0.1110 (2)	0.044 (2)
O(2)	0.5306 (5)	0.3248 (8)	0.1754 (2)	0.045 (2)
O(3)	0.2924 (5)	0.2937 (8)	0.1415 (2)	0.049 (2)
O(4)	0.3501 (5)	−0.0234 (8)	0.0710 (2)	0.048 (2)
N(1)	0.4764 (5)	0.3744 (10)	0.0449 (2)	0.038 (3)
C(1)	0.6859 (8)	0.0008 (12)	0.1442 (4)	0.043 (3)
C(2)	0.7119 (8)	0.1277 (13)	0.1877 (3)	0.050 (3)
C(3)	0.6327 (9)	0.2784 (13)	0.2006 (3)	0.047 (4)
C(4)	0.7832 (10)	−0.1578 (16)	0.1322 (5)	0.066 (4)
C(5)	0.6640 (11)	0.4042 (19)	0.2519 (5)	0.083 (5)
C(6)	0.1850 (9)	0.2410 (13)	0.1264 (3)	0.045 (3)
C(7)	0.1490 (8)	0.0866 (13)	0.0899 (4)	0.051 (3)
C(8)	0.2341 (9)	−0.0342 (13)	0.0656 (3)	0.044 (3)
C(9)	0.0808 (10)	0.3608 (20)	0.1530 (5)	0.078 (5)
C(10)	0.1855 (10)	−0.2064 (16)	0.0295 (5)	0.066 (5)
C(11)	0.5066 (7)	0.5632 (13)	0.0523 (3)	0.043 (3)
C(12)	0.4693 (7)	0.3124 (11)	−0.0082 (4)	0.041 (3)

Table 2. *Geometric parameters* (Å, °)

Cu(1)—O(1)	1.963 (5)	Cu(1)—O(2)	1.938 (5)
Cu(1)—O(3)	1.956 (6)	Cu(1)—O(4)	1.946 (5)
Cu(1)—N(1)	2.248 (6)	O(1)—C(1)	1.267 (10)
O(2)—C(3)	1.263 (10)	O(3)—C(6)	1.243 (11)
O(4)—C(8)	1.249 (11)	N(1)—C(11)	1.327 (11)
N(1)—C(12)	1.326 (10)	C(1)—C(2)	1.362 (12)
C(1)—C(4)	1.536 (13)	C(2)—C(3)	1.373 (12)
C(3)—C(5)	1.508 (15)	C(6)—C(7)	1.398 (12)
C(6)—C(9)	1.546 (15)	C(7)—C(8)	1.377 (13)
C(8)—C(10)	1.521 (13)	C(11)—C(12*A*)	1.378 (12)
C(12)—C(11*A*)	1.378 (12)		
O(1)—Cu(1)—O(2)	91.3 (2)	O(1)—Cu(1)—O(3)	163.9 (2)
O(2)—Cu(1)—O(3)	85.9 (2)	O(1)—Cu(1)—O(4)	87.4 (2)
O(2)—Cu(1)—O(4)	168.5 (2)	O(3)—Cu(1)—O(4)	92.1 (2)
O(1)—Cu(1)—N(1)	99.1 (2)	O(2)—Cu(1)—N(1)	96.8 (2)
O(3)—Cu(1)—N(1)	97.0 (2)	O(4)—Cu(1)—N(1)	94.7 (2)
Cu(1)—O(1)—C(1)	124.5 (5)	Cu(1)—O(2)—C(3)	125.0 (5)
Cu(1)—O(3)—C(6)	124.6 (5)	Cu(1)—O(4)—C(8)	125.7 (5)
Cu(1)—N(1)—C(11)	122.8 (5)	Cu(1)—N(1)—C(12)	121.6 (5)
C(11)—N(1)—C(12)	115.6 (7)	O(1)—C(1)—C(2)	128.0 (8)
O(1)—C(1)—C(4)	114.2 (7)	C(2)—C(1)—C(4)	117.8 (8)
C(1)—C(2)—C(3)	122.1 (8)	O(2)—C(3)—C(2)	127.9 (8)
O(2)—C(3)—C(5)	113.2 (8)	C(2)—C(3)—C(5)	118.9 (8)
O(3)—C(6)—C(7)	128.0 (8)	O(3)—C(6)—C(9)	114.5 (8)
C(7)—C(6)—C(9)	117.5 (8)	C(6)—C(7)—C(8)	122.3 (8)
O(4)—C(8)—C(7)	127.2 (8)	O(4)—C(8)—C(10)	114.5 (8)
C(7)—C(8)—C(10)	118.2 (8)	N(1)—C(11)—C(12*A*)	122.8 (7)
N(1)—C(12)—C(11*A*)	121.6 (7)		

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and geometry involving fluorine have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71112 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1035]

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The Monopotassium Salt of the Ligand of a Ziegler–Natta Catalyst

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Abstract

The anion of dipotassium (*tert*-butylamino)dimethyl(tetramethylcyclopentadienyl)silanediide can coordinate to transition metals to form precursors for single-component Ziegler–Natta polymerization catalysts. The related monoanion derivative potassium (*tert*-butylamino)dimethyl(tetramethylcyclopentadienyl)silanide tetrahydrofuran solvate has been isolated as the first crystalline salt of this important ligand family. The tetramethylcyclopentadienyl group in the crystal has a potassium ion on each face, 2.8 Å from the center of the five-membered ring; each K atom is bonded to two rings and one tetrahydrofuran solvent molecule.

Comment

The organoscandium complexes $[\{(C_5Me_4)SiMe_2(NCMe_3)\}ScR]_2(PMe_3)_x$ (R = H, $CH_2CH_2CH_3$; x = 2, 0) are the first compounds which catalyze the homogeneous Ziegler–Natta polymerization of

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† Contribution No. 8735