C6	−0.2994 (4)	−0.0120 (3)	0.5589 (4)	0.0603 (19)
C7	−0.2112 (5)	−0.0645 (4)	0.3508 (4)	0.069 (2)
C8	−0.0278 (5)	−0.2492 (4)	0.3651 (4)	0.079 (2)
C9	−0.0062 (5)	−0.3104 (3)	0.5790 (4)	0.0617 (19)
C10	−0.1809 (5)	−0.1630 (4)	0.6980 (3)	0.0590 (19)
C11	0.0704 (4)	0.0528 (3)	0.4505 (3)	0.0330 (14)
C12	0.0319 (4)	0.0631 (3)	0.5470 (3)	0.0443 (16)
C13	0.1033 (4)	−0.0035 (3)	0.6004 (3)	0.0473 (17)
C14	0.1701 (4)	−0.0675 (4)	0.5404 (3)	0.0430 (16)
C15	0.1585 (4)	−0.0282 (3)	0.4461 (3)	0.0387 (14)
C16	0.1920 (4)	−0.0408 (3)	0.3504 (3)	0.0443 (17)
C17	0.1241 (5)	0.0280 (3)	0.2974 (3)	0.0510 (16)
C18	0.0518 (4)	0.0874 (3)	0.3570 (3)	0.0443 (17)
C19	0.3858 (5)	0.1455 (3)	0.4647 (3)	0.0457 (17)
C20†	0.409 (2)	0.1248 (19)	0.5653 (7)	0.075 (10)
C20'†	0.4075 (14)	0.1190 (15)	0.5633 (8)	0.048 (8)
C21†	0.328 (3)	0.1853 (18)	0.6232 (18)	0.046 (7)
C21'†	0.325 (3)	0.181 (2)	0.6091 (19)	0.068 (9)
C22†	0.259 (2)	0.2387 (19)	0.5596 (7)	0.057 (8)
C22'†	0.2564 (17)	0.253 (2)	0.5554 (8)	0.039 (6)
C23	0.2951 (4)	0.2226 (3)	0.4607 (3)	0.0413 (16)
C24	0.2743 (5)	0.2477 (3)	0.3664 (3)	0.0537 (18)
C25	0.3564 (6)	0.1860 (4)	0.3128 (4)	0.066 (2)
C26	0.4237 (5)	0.1222 (4)	0.3723 (4)	0.060 (2)

† Site occupancy = 0.50.

Table 2. *Selected geometric parameters (Å, °)*

Co—C13	2.023 (4)	Fe—C17	2.011 (5)
Co—C12	2.052 (4)	Fe—C18	2.026 (4)
Co—C14	2.054 (4)	Fe—C25	2.029 (5)
Co—C1	2.071 (4)	Fe—C24	2.044 (4)
Co—C3	2.077 (5)	Fe—C16	2.049 (4)
Co—C2	2.078 (5)	Fe—C26	2.054 (5)
Co—C4	2.081 (4)	Fe—C19	2.055 (5)
Co—C5	2.122 (4)	Fe—C23	2.056 (4)
Co—C11	2.278 (4)	Fe—C11	2.100 (4)
Co—C15	2.296 (4)	Fe—C15	2.120 (4)
C12—Co—C1	108.6 (2)	C17—Fe—C25	109.4 (2)
C14—Co—C4	112.1 (2)	C18—Fe—C24	105.2 (2)
C13—Co—C5	116.3 (2)	C16—Fe—C26	109.1 (2)
C2—Co—C11	105.4 (2)	C23—Fe—C11	106.8 (2)
C3—Co—C15	107.5 (2)	C19—Fe—C15	109.1 (2)

The Co- and Fe-atom positions were determined by the Patterson method and the remaining non-H atoms were found from $\Delta\rho$ maps. The assignment of the heavy atoms as Co and Fe was performed using the different chemical environments known from the synthetic work. All H atoms were included at calculated positions and refined using a riding model, with isotropic displacement parameters equal to $1.2U_{\rm eq}$ of the attached C atom. The occupancies of the disordered C20–C22 atoms were not refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1995). Software used to prepare material for publication: *PLATON*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1392). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Restricting Chelate Ring Flipping in Cu$^{\rm II}$ Complexes. I. Non-Thermochromic Bis(*o*-phenylenediamine-*N*,*N'*)copper(II) Bis(tetrafluoroborate)

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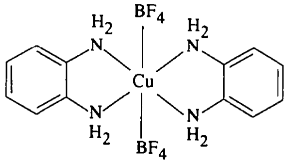
Abstract

The title complex, $[Cu(C_6H_8N_2)_2](BF_4)_2$, is the first in a series where the phenylenediamine collar restricts the 'flipping' of the chelate ring C atoms, which is the mechanism responsible for the thermochromic transition in *N*,*N*-diethylethylenediamine complexes. The Cu$^{\rm II}$ ion has tetragonally distorted octahedral geometry, with four short equatorial Cu—N bonds [2.023 (3) and 1.990 (3) Å] and two long mutually *trans* axial Cu···F interactions [2.546 (2) Å]. The features of the molecular packing, namely the shorter metal-to-anion contacts and the stronger N—H···F hydrogen bonds compared with those in the thermochromic analogues, seem to be associated with non-thermochromic behaviour.

Comment

Complexes of copper and nickel with *N*,*N*-diethylenediamine exhibit reversible first-order thermochromic phase transitions (Bloomquist & Willett, 1982). Variable-temperature single-crystal X-ray studies of [Cu(*N*,*N*-diethylethylenediamine)$_2$](ClO$_4$)$_2$ carried out by

Grenthe, Paoletti, Sandstrom & Glikberg (1979) revealed the unique mechanism of the colour change, *i.e.* a dynamic inversion of the chelate ring 'switches on' in the crystal at 317 K, reducing the strength of the Cu—N bonds. In order to assess the contribution of this 'flip-flop' factor, we have synthesized a series of *N*,*N*-dialkyl-substituted diamine complexes in which chelate ring C atoms are prevented from undergoing such inversion. The title compound, (I), is the first in this series and it shows no colour change between 77 and 458 K.



(I)

The Cu^{II} ion, situated on a crystallographic centre of symmetry, has a tetragonally distorted octahedral environment, with four equatorial Cu—N bonds [Cu—N1 2.023 (3) and Cu—N2 1.990 (3) Å] and two long axial Cu···F1 distances [2.546 (2) Å], similar to those observed in $[Cu(ethylenediamine)_2](BF_4)_2$ (Brown, Lee & Melson, 1968). The identification of the H atoms in the difference Fourier synthesis and the presence of two BF_4^- anions establishes that the ligand is neutral, although it has also been found in the deprotonated form (Hall & Soderberg, 1968). The Cu—N bonds differ in the title compound, although both N atoms of the ligand are equivalent (unsubstituted); distortions of the Cu—N bond are known in the case of alkyl substitutions on the N atom, with the Cu—N(secondary) bond being significantly longer compared with the Cu—N(primary) bond (Narayanan & Bhadbhade, 1996; Grenthe, Paoletti, Sandstrom & Glikberg, 1979). The bite angle [N1—Cu1—N2 84.72 (14)°], however, seems to be unaffected by the substitution. Asymmetry in the Cu—N bonds is a feature of thermochromic complexes. The Cu–anion interactions were initially believed to be directly responsible for the thermochromic transitions in asymmetric *N*,*N*-dialkyl ethylenediamine complexes (Pfeiffer & Glaser, 1938) and have been studied extensively using IR, EPR (electron paramagnetic resonance) and NMR spectroscopic techniques (Yokoi, Sai & Isobe, 1969; Pylkki, Willett & Dodgen, 1984). X-ray data on thermochromic complexes, however, revealed the metal-to-anion distances to be more than 3.6 Å (Grenthe, Paoletti, Sandstrom & Glikberg, 1979; Narayanan & Bhadbhade, 1996), suggesting an indirect involvement of anions in phase transitions. The Cu···F1 distance in the title compound is only 2.546 (2) Å; this separation is observed to increase when bulkier substituents are placed on the N atom. Chains of molecules run with their longer axis almost parallel to the *b* axis.

Only one H atom from each of the N1 and N2 atoms is involved in strong hydrogen-bonding interactions with the F atoms of the anions. One interaction is intermolecular [F4···N2^i 2.963 (5), F4···H2N2 2.301 Å and F4···H2N2—N2^i 157.4°; symmetry code: (i) $2-x$, $1-y$, $-z$], the other intramolecular [F3···N1 2.928 (5), F3···H2N1 2.245 Å and F3···H2N1—N1 158.0 Å]. These strong hydrogen-bonding interactions, combined with closer metal-to-anion distances, appear to create conditions uncongenial to thermochromic transitions as observed in the structure of non-thermochromic $[Cu(N,N\text{-dimethylethylenediamine})_2](NO_3)_2$ (Narayanan & Bhadbhade, 1995). The intermolecular interactions generated by varying alkyl substitutions on the N and C atoms of the ligand are being studied in order to understand the role of the flexibility of the ethylenediamine moiety in thermochromic behaviour.

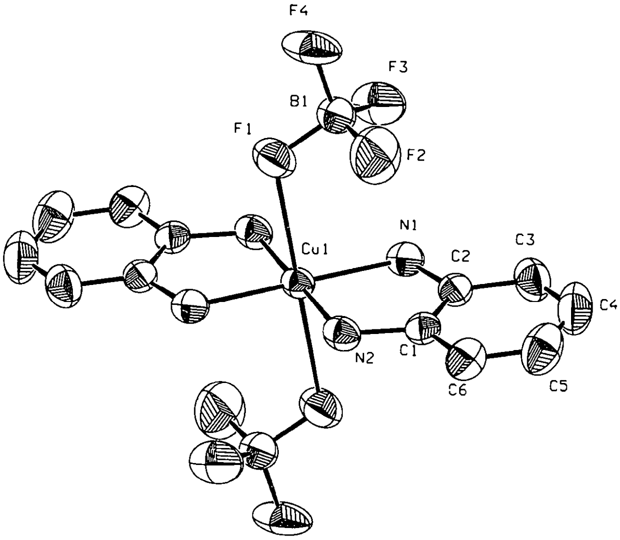


Fig. 1. An *ORTEP*II (Johnson, 1976) view of the title molecule showing the atom-labelling scheme and 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

Experimental

The title complex was synthesized by adding a solution of copper tetrafluoroborate (1 mmol, 0.238 g) in ethanol (5 ml) to a solution of *o*-phenylenediamine (2 mmol, 0.216 g) in ethyl acetate (20 ml). Recrystallization from ethanol yielded crystals suitable for X-ray analysis.

Crystal data

$[Cu(C_6H_8N_2)_2](BF_4)_2$
$M_r = 453.45$
Orthorhombic
Pbca
$a = 7.974\,(2)$ Å
$b = 21.692\,(4)$ Å
$c = 10.038\,(7)$ Å
$V = 1736.3\,(13)$ Å^3
$Z = 4$
$D_x = 1.735$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 9$–$14°$
$\mu = 1.343$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.24 × 0.12 × 0.03 mm
Blue–violet

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
1360 measured reflections
1360 independent reflections
894 observed reflections $[I > 2\sigma(I)]$
$\theta_{\rm max} = 24°$
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0346$
$wR(F^2) = 0.1014$
$S = 0.991$
1356 reflections
157 parameters
$w = 1/[\sigma^2(F_o^2) + (0.062P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.40$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1992)
Extinction coefficient: 0.0017 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu1	1/2	1/2	0	0.0344 (2)
N1	0.5492 (5)	0.4419 (2)	−0.1527 (3)	0.0425 (8)
N2	0.3791 (5)	0.4284 (2)	0.0784 (3)	0.0433 (8)
C1	0.3868 (4)	0.3753 (2)	−0.0092 (3)	0.0397 (8)
C2	0.4755 (4)	0.3819 (2)	−0.1262 (3)	0.0396 (8)
C3	0.4945 (6)	0.3317 (2)	−0.2101 (5)	0.0570 (11)
C4	0.4246 (7)	0.2760 (2)	−0.1741 (6)	0.0745 (15)
C5	0.3326 (7)	0.2701 (2)	−0.0587 (5)	0.0706 (13)
C6	0.3130 (6)	0.3200 (2)	0.0243 (4)	0.0536 (11)
B1	0.8680 (6)	0.4293 (2)	0.0779 (4)	0.0481 (11)
F1	0.7765 (3)	0.47971 (10)	0.1191 (2)	0.0633 (7)
F2	0.7741 (4)	0.37888 (12)	0.1097 (3)	0.1020 (10)
F3	0.8953 (3)	0.43265 (13)	−0.0573 (2)	0.0833 (8)
F4	1.0173 (3)	0.42870 (15)	0.1456 (3)	0.0825 (9)

Table 2. *Selected geometric parameters (Å, °)*

Cu1—F1	2.546 (2)	Cu1—N1	2.023 (3)
Cu1—N2	1.990 (3)		
N2—Cu1—N1	84.72 (14)	N1—Cu1—F1	94.61 (13)
N2—Cu1—F1	95.67 (14)		

H atoms were located in a ΔF synthesis and refined with isotropic displacement parameters. Although ideally an absorption correction should have been applied, this was not possible. The satisfactory values of the the R indices and ΔF residuals, however, combined with the low uncertainties in the molecular-geometry parameters, suggest that any significant effects are limited to the displacement parameters.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe *et al.*, 1992). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1992).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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