Inorganica Chimica Acta, *105* (1985) 13–17

Coordination Behavior of 2-Aminobenzophenone Toward the Copper(II) Ion in the Presence of Low-coordinating Coligands

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Received February 2, 1985

Abstract

A compound of the type Cu(2-aminobenzophenone)$_2$(BF$_4$)$_2$ was prepared and characterized by means of structural and vibrational measurements. Coordination around the copper, lying on the center of symmetry, involves two centrosymmetric ligand molecules, which act as bidentate through the carbonyl oxygen and amine nitrogen atoms (Cu–O = 1.956(2) Å, Cu–N = 1.984(4) Å).

Two fluorine atoms of two BF_4^- anions occupy the fifth and sixth coordination positions, forming an elongated tetragonal bipyramid (Cu–F = 2.468(3) Å).

Spectroscopic measurements carried out on fluoroborate and perchlorate complexes show that they are isomorphous and isostructural.

Introduction

Benzophenone and its derivatives, which are intermediates in several syntheses of pharmaceuticals [1, 2] and are very efficient sensitisers in photoreactions [3, 4], are also very interesting from a coordinative point of view since they contain both a hetero-atom and a π-donor system. They may act as either n or π donors, depending on the particular metal centre with which they interact [5, 6].

The introduction of another potential binding site, such as an amino group in the ortho-position, strongly modifies the coordinating ability of benzophenone, making it a potentially bidentate ligand.

Previous works, however, have reported conflicting results: 2-aminobenzophenone (2-abf) has been found to act essentially as monodentate through the amino group towards HgBr$_2$ in the (HgBr$_2$)$_2$(2-abf) adduct [7], and simultaneously as monodentate (through the amino group) and bidentate (through amino and carbonyl group) towards CuX$_2$ (X = Cl, Br) in the CuX$_2$(2-abf)$_2$ compounds [8], probably due to the presence of strongly coordinating coligands such as the halide ions.

In order to verify the real coordinating ability of 2-aminobenzophenone in the presence of coligands of low coordinating properties we prepared and characterized by means of magnetic and spectroscopic measurements the Cu(2-abf)$_2$X$_2$ (X = ClO$_4$, BF$_4$) compounds. For one of them, Cu(2-abf)$_2$(BF$_4$)$_2$, the X-ray crystal structure was also determined.

Experimental

Preparation of the Complexes

Both complexes of formula CuX$_2$L$_2$ (L = 2-aminobenzophenone and X = BF$_4$, ClO$_4$) were prepared by adding an ethanolic copper(II) fluoroborate or perchlorate solution (1 mM) to an ethanolic ligand solution (1 mM). On standing, the crystals were separated after a few days. *Anal.* Found: C, 49.22; H, 3.51; N, 4.45. Calc. for $C_{26}H_{22}B_2F_8N_2O_2Cu$ (green-brown): C, 49.32; H, 3.48; N, 4.48%. Found: C, 47.41; H, 3.36; N, 4.30. Calc. for $C_{26}H_{22}Cl_2N_2O_{10}Cu$ (green-brown): C, 47.49; H, 3.34; N, 4.26%.

Physical Measurements

The electronic spectra of the solid compounds were recorded on a SHIMADZU MPS 50L spectrophotometer. Samples were prepared by grinding the complexes on filter paper as support. The infrared spectra in KCl or KBr pellets or in nujol mulls on KCl or KBr pellets as support (4000–400 cm^{-1}), and in nujol mulls on polythene as support (600–100 cm^{-1}), were recorded on a Perkin-Elmer 180 spectrophotometer.

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0020-1693/85/$3.30

TABLE I. Experimental Data for the Crystallogaphic Analysis.

Formula	$C_{26}H_{22}B_2CuF_8N_2O_2$
M.W.	631.63
Space group	$P2_1/c$
a (Å)	13.540(3)
b (Å)	7.772(1)
c (Å)	12.858(2)
β (°)	109.00(2)
V (Å^3)	1279.4(4)
Z	2
D_{calc} (g cm^{-3})	1.64
D_{obs} (g cm^{-3})	1.62 (by flotation)
Crystal data radiation	Ni-filtered CuKα
wavelength (Å)	1.54178
$F(000)$	638
temperature (°C)	20 ± 2
Crystal size (mm)	0.10 × 0.33 × 0.36
diffractometer	Siemens AED
μ (cm^{-1})	19.79
scan speed	2.5° min^{-1}
scan width	$1.20 + 0.35\ \mathrm{tg}\theta$
radiation	Cu Kα
θ range (°)	3–60
scan mode	$\omega-2\theta$
no. of measured reflections	2141
condition for observed reflections	$I > 2\sigma(I)$ $[\sigma^2(I) = (\text{total counts}) + (0.01 \times \text{intens})^2]$
no. of reflections used in the refinement	1557
no. of refined parameters	231
$R = \Sigma\lvert\Delta F\rvert\lvert\,\Sigma\lvert F_o\rvert$	0.0367
$R_w = [\Sigma w(\Delta F)^2/\Sigma F_o^2]^{1/2}$	0.0407
k, g $(w = k[\sigma^2(F_o) + gF_o^2])$	1, 0.04055

The EPR spectra of polycrystalline samples were recorded on a Varian E9 X-Band spectrometer. The spectra were calibrated with diphenyl picrylhydrazyl (DPPH, g = 2.0036) as a field marker. Thermal and calorimetric analyses were performed on Mettler TA 3000 and Perkin-Elmer DSC2 instruments, respectively.

X-Ray Data Collection and Structure Determination

Intensity data were collected by mounting a crystal with the c axis coincident with the ϕ axis of an automated Siemens AED single-crystal diffractometer. Cell parameters were obtained from a least-squares refinement of the θ values of 20 reflections accurately measured on the same diffractometer. Crystal data and details of data collection are quoted in Table I. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by Wilson's method and refined by least-squares.

No correction for absorption was applied in view of the low absorbance of the sample.

The structure was solved by the heavy-atom method, starting from a three-dimensional Patterson map. The positions of all non-hydrogen atoms were revealed by the subsequent Fourier synthesis phased on the contribution of the Cu atom.

The refinement was carried out by least-squares full-matrix cycles using the SHELX [9] system of computer programs, firstly with isotropic thermal parameters, then with anisotropic thermal parameters for non-hydrogen atoms. A difference Fourier map revealed all hydrogen atoms, which were introduced in the calculation and refined isotropically. The function minimized in the least squares calculations was $\Sigma w|\Delta F|^2$; unit weights were used in the first cycles of refinement, the weight calculated as $w = 1/\sigma^2(F_o)\ 0.004055\ F_o^2$ was chosen in the final cycles. The atomic scattering factors were taken from the International Tables [10]. The final R and R_w values were 0.0367 and 0.0407 respectively (observed reflections only).

The atomic fractional coordinates are given in Tables II and III; lists of thermal parameters and of the observed and calculated structure factors are available from the authors on request.

Calculations were performed on a CYBER 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, Bologna, with the financial support from the University of Parma.

TABLE II. Fractional Atomic Coordinates (×10^4) for Non-hydrogen Atoms, with e.s.d.s in Parentheses.

	x/a	*y/b*	*z/c*
Cu	0	0	0
O	1330(2)	0767(4)	1043(2)
N	389(3)	1295(5)	−1139(3)
C(1)	2172(3)	919(5)	853(3)
C(2)	2255(3)	646(5)	−253(3)
C(3)	3196(3)	41(5)	−349(4)
C(4)	3276(4)	−421(6)	−1360(4)
C(5)	2414(4)	−256(6)	−2291(4)
C(6)	1477(4)	338(6)	−2227(4)
C(7)	1380(3)	778(5)	−1214(3)
C(8)	3112(3)	1297(5)	1808(3)
C(9)	3147(3)	615(6)	2824(3)
C(10)	4023(3)	874(6)	3732(4)
C(11)	4851(3)	1813(6)	3644(3)
C(12)	4802(3)	2550(6)	2644(4)
C(13)	3934(3)	2295(6)	1727(4)
B	−1440(4)	3988(7)	410(4)
F(1)	−959(3)	2687(4)	39(3)
F(2)	−1170(3)	5532(4)	30(3)
F(3)	−2492(2)	3801(5)	23(2)
F(4)	−1105(3)	3992(6)	1537(2)

TABLE III. Fractional Atomic Coordinates (×10^3) for Hydrogen Atoms.

	x/a	*y/b*	*z/c*
H(1)	380(4)	−1(6)	37(4)
H(2)	397(4)	−81(7)	−144(4)
H(3)	248(4)	−52(7)	−304(4)
H(4)	82(4)	45(6)	−286(4)
H(5)	−13(4)	125(7)	−172(5)
H(6)	42(4)	218(8)	−84(4)
H(7)	262(5)	42(6)	294(4)
H(8)	406(4)	31(7)	448(5)
H(9)	550(4)	206(6)	434(4)
H(10)	538(4)	313(7)	259(4)
H(11)	388(4)	294(7)	101(4)

TABLE IV. Bond Distances (Å) and Angles (deg).

Cu–O	1.956(2)	O–Cu–N	86.9(1)
Cu–N	1.984(4)	F(1)–Cu–N	81.6(1)
Cu–F(1)	2.468(4)	F(1)–Cu–O	95.8(1)
F(1)–B	1.370(7)	F(1)–B–F(2)	107.8(4)
F(2)–B	1.389(7)	F(1)–B–F(3)	110.8(4)
F(3)–B	1.355(6)	F(1)–B–F(4)	109.8(4)
F(4)–B	1.370(6)	F(2)–B–F(3)	109.2(4)
		F(2)–B–F(4)	109.6(4)
		F(3)–B–F(4)	109.6(4)
O–C(1)	1.247(5)	C(5)–C(6)	1.377(8)
N–C(7)	1.434(6)	C(6)–C(7)	1.394(7)
C(1)–C(2)	1.478(6)	C(8)–C(9)	1.396(6)
C(1)–C(8)	1.482(5)	C(8)–C(13)	1.388(6)
C(2)–C(3)	1.401(6)	C(9)–C(10)	1.382(5)
C(2)–C(7)	1.410(5)	C(10)–C(11)	1.373(6)
C(3)–C(4)	1.386(7)	C(11)–C(12)	1.389(7)
C(4)–C(5)	1.379(6)	C(12)–C(13)	1.382(5)
O–C(1)–C(8)	116.7(4)	N–C(7)–C(6)	120.4(4)
O–C(1)–C(2)	112.4(4)	N–C(7)–C(2)	120.0(4)
C(2)–C(1)–C(8)	120.8(4)	C(1)–C(8)–C(13)	122.8(4)
C(1)–C(2)–C(7)	121.8(4)	C(1)–C(8)–C(9)	117.3(4)
C(1)–C(2)–C(3)	119.3(4)	C(9)–C(8)–C(13)	119.9(4)
C(3)–C(2)–C(7)	118.4(4)	C(8)–C(9)–C(10)	119.6(4)
C(2)–C(3)–C(4)	121.4(4)	C(9)–C(10)–C(11)	120.5(4)
C(3)–C(4)–C(5)	119.2(5)	C(10)–C(11)–C(12)	120.1(4)
C(4)–C(5)–C(6)	121.0(5)	C(11)–C(12)–C(13)	120.1(4)
C(5)–C(6)–C(7)	120.4(5)	C(8)–C(13)–C(12)	119.8(4)
C(2)–C(7)–C(6)	119.6(4)		

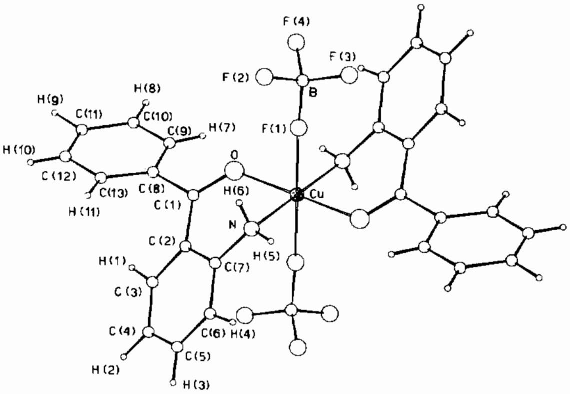

Fig. 1. The structure of the Cu(2abf)$_2$(BF$_4$)$_2$ complex.

Results and Discussion

Description of the Structure

As shown in Fig. 1, the copper atom lying on the symmetry center is surrounded by two centrosymmetric ligand molecules in a square planar arrangement. Two fluorine atoms from two tetrafluoroborate anions occupy the fifth and sixth coordination positions, forming an elongated tetragonal bipyramid. Distances and angles are quoted in Table IV.

One of the most relevant structural features is the strict bidentate coordination of the ligand through the carbonyl oxygen and amino nitrogen atoms in the equatorial plane (Cu–O = 1.956(2) Å, Cu–N = 1.984(4) Å) to the metal ion. In the halide adducts, the coordinative behavior of 2abf was different: in (HgBr$_2$)$_2$·2abf [7], the ligand is essentially coordinated through the nitrogen atom (Hg–N = 2.51(3) Å), the Hg–O distance being 3.04(2) Å. In the CuCl$_2$(2abf)$_2$ adduct [8], one ligand molecule acts as monodentate (Cu–N = 2.020(4) Å) and the second one as bidentate (Cu–N = 2.028(3), Cu–O = 2.256(3) Å).

In the present work the ligand acts as bidentate, therefore its coordinative behavior may be considered as being strictly dependent on the co-ligands. With strongly coordinating co-ligands, it essentially acts as monodentate; with weakly coordinating co-ligands (such as BF_4^-) as truly bidentate.

Another relevant structural feature is the presence of long bonded BF_4 groups (Cu–F(1) 2.468(3) Å). The weak coordination of tetrafluoroborate is in agreement with its coordinative properties which are known to be negligible, generally existing as uncoordinated tetrahedral anion, as a consequence of the high electronegativity of the fluorine atoms [11]. The Cu–F(1) distance is consistent with the semicoordination of the BF_4 anion [12] and BF_4^- is an almost regular tetrahedron in accord with what has been found hitherto in semicoordinated disordered unidentate BF_4^- anions [13].

As regards the coordination polyhedron, the four atoms in the equatorial plane are co-planar for the symmetry requirement, the distortion of the bipyramid being measured by the angle between Cu–F(1) and the normal to the equatorial plane (10.5(1)°). The phenyl rings are planar (Table V) and themselves form a dihedral angle of 125.4(1)° and 25.4(2)° and 145.5(2)° with the carbonyl group. In the free 2abf molecule [14] the corresponding dihedral angles are 67.6, 19.1 and 56.1°. The conformation of the chelation ring can be described by

TABLE V. Equations of Least-squares Planes, with Distances (Å) of Relevant Atoms from the Planes given in Brackets.

Plane A	C(2), C(3), C(4), C(5), C(6), C(7) $0.32371x + 0.93781y - 0.12542z = 1.52855^a$ [N −0.086(4), C(1) −0.152(4)]
Plane B	C(8), C(9), C(10), C(11), C(12), C(13) $0.51799x - 0.82669y - 0.21970z = 0.45862$ [O −0.523(3), C(1) 0.061(4)]
Plane C	O, C(1), C(2), C(8) $-0.11115x + 0.97665y - 0.18387z = 0.20163$

[a] *x, y, z* are the orthogonal coordinates.

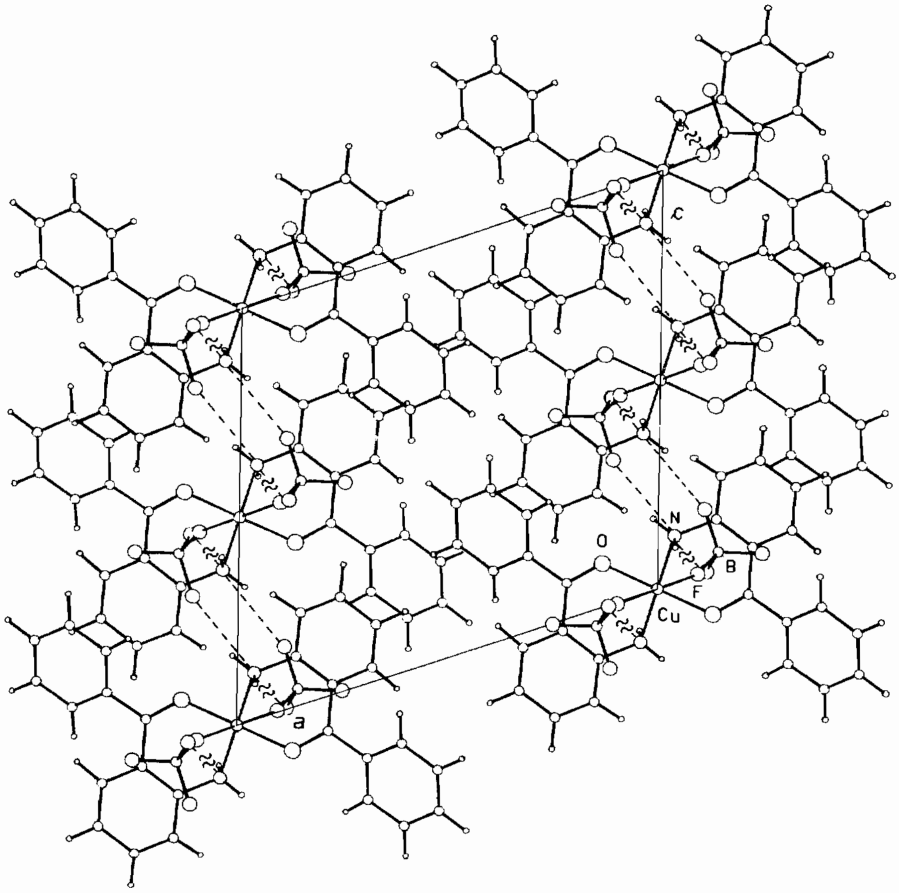

Fig. 2. Projection of the structure along [010].

using torsion angles: Cu–N–C(7)–C(2) −48.7(5)°; N–C(7)–C(2)–C(1) 4.0(6)°; C(7)–C(2)–C(1)–O 22.0(6)°; Cu–O–C(1)–C(2) 4.7(6)°. The ligand C–N and C–O bonds, 1.360 and 1.231(4) Å [14] are lengthened by coordination to the metal, as they are of 1.434(6) and 1.247(5) Å, respectively, in Cu-(2-abf)$_2$(BF$_4$)$_2$.

The $-NH_2$ group participates in hydrogen bonds (Fig. 2) with the fluorine atoms: N···F(4)^{i} = 3.022(4) Å (i = $\bar{x}$, ½ − y, z − ½), N–H(5) = 0.84(5) Å, H(5)···F(4)^{i} = 2.20(6) Å, N–H(5)···F(4)^{i} = 163(6)°, N···F(2)^{ii} = 2.872(5) Å (ii = $\bar{x}$, 1 − y, −z), N–H(6) = 0.78(6) Å, H(6)···F(2)^{ii} = 2.15(6) Å, N–H(6)···F(2)^{ii} = 155(6)°. In uncoordinated or monodentate 2abf molecules, the amine nitrogen atom is involved in a strong intramolecular hydrogen bond with the carbonyl oxygen atom (NH····O = 2.713(3) and 2.772(2) Å, respectively), whereas in this complex this is absent, since both atoms are simultaneously involved in the coordination.

TABLE VI. Room Temperature Spectroscopic Data of the Solid Complexes.

	[Cu(2abf)$_2$(BF$_4$)$_2$]	[Cu(2abf)$_2$(ClO$_4$)$_2$]
$g_\parallel$	2.291	2.282
$g_\perp$	2.073	2.060
$A_\parallel$ (cm^{-1}) × 10^4	192	170
d–d max (cm^{-1})	17.480	17.240
ν_3 (cm^{-1})	1120m	1150m
	1075vs	1115vs
	1020vs	1080vs
ν_1 (cm^{-1})	750s	940s
ν_4 (cm^{-1})	515w	638s
		625s

EPR and Spectroscopic Results of Fluoroborate and Perchlorate Complexes

The room-temperature EPR parameters, as well as the d–d bands of the fluoroborate compound (Table VI), in agreement with the structural results, are typical of distorted elongated tetragonal bipyramidal complexes with a $d_{x^2-y^2}$ ground state. The greater g values and lower d–d band maximum position in our compound with respect to those of the structurally similar Cu(en)$_2$(BF$_4$)$_2$ [12, 15] are consistent with the different chromophore (CuN$_2$O$_2$F$_2$ in our complex and CuN$_4$F$_2$ in the other).

The infrared spectrum of the compound in the polyanion region (Table IV) shows evidence of semicoordination of the fluoborate anions, although X-ray analysis demonstrates a low tetrahedral distorsion of BF$_4^-$.

The perchlorate compound shows a powder X-ray diffraction pattern similar to that of the fluoroborate one, an infrared spectrum (Table VI) consistent with the presence of semicoordinated polyanions [13, 16] and identical to that of fluoroborate compound in the other spectral regions, and electronic and EPR spectra slightly different from those of the fluoroborate compound, in agreement with the presence of a different chromophore (CuN$_2$O$_4$ in the compound). In view of all the above we conclude that fluoroborate and perchlorate compounds are isomorphous and isostructural.

TG and DSC measurements performed on both compounds show the absence of thermochromic behavior: the compounds are stable until their melting points (about 250 °C), indicating that the low ligand field in plane stabilization favours axial coordination.

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