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Copper(II) Halide Complexes of 2-Aminobenzophenone. Crystal and Molecular Structure of Bis(2-aminobenzophenone)dichlorocopper(II)

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The complexes CuX_2L_2 ($X = Cl, Br$; L = 2-aminobenzophenone) were prepared and characterized by means of magnetic and spectroscopic measurements. For the Cl compound the crystal structure was also determined. Crystals are triclinic, space group $P\bar{1}$, with $a = 13.397(3)$, $b = 10.752(2)$, $c = 9.205(2)$ Å, $\alpha = 72.26(1)°$, $\beta = 91.58(1)°$, $\gamma = 106.86(1)°$, and $Z = 2$. The structure was solved by the heavy-atom method and refined by least-squares calculations to $R = 0.034$ for 2581 counter data. It consists of discrete CuX_2L_2 monomers showing distorted trigonal bipyramidal coordination geometry about the copper ion. The amino nitrogens are axial ligands, with the equatorial positions occupied by two chlorine atoms and a carbonyl oxygen from one L molecule acting as a bidentate ligand. Infrared and ligand field spectroscopies and magnetic measurements, interpreted on the basis of the known crystal structure, also suggest a similar structure for the related Br compound.

Introduction

Metal ions form stable complexes with ligands containing a carbonyl group as monofunctional ketones, which generally are σ-bonded through the oxygen atom [1–6].

Among these ligands benzophenone, although little investigated, appears very interesting presenting a variable coordinating behavior. In fact it was found to coordinate through the carbonyl oxygen to lithium ions forming a three-center bonding, through the π-electron systems of the aromatic rings to the VA group trihalides [7–9] or through the π-electron system of the carbonyl group to zerovalent nickel [10, 11].

The presence on the benzophenone of another potential binding site, as an amino group, seems to decrease the coordinating ability of the carbonyl group, as found in its 4-amino derivative resulting in the amino group being generally preferred for the coordination to metal ions [12, 13]. Furthermore, for this derivative π-interactions through the aromatic rings with metal halides were also suggested [12, 13].

Being particularly interested in this field we have now investigated the coordinative behaviour of 2-aminobenzophenone, a ligand which, for the position of the amino group, also presents the possibility to form 6-membered chelate rings. In particular in this paper we report a magnetic and spectroscopic investigation on its solid complexes with copper(II) halides. For one of them, bis(2-aminobenzophenone)dichlorocopper(II), the crystal structure has also been determined.

Experimental

Preparation of the complexes

Both complexes of formula CuX_2L_2 (L = 2-aminobenzophenone and X = Cl, Br) were prepared by adding an ethanolic copper(II) halide solution (1 m*M*) to an ethanolic ligand solution (1 or 2 m*M*). On standing for some hours, crystals precipitated. Found: C, 58.81; H, 4.13; N, 5.28. Calcd. for $C_{26}H_{22}Cl_2CuN_2O_2$ (green): 58.99; H, 4.16; N, 5.29. Found: C, 50.46; H, 3.50; N, 4.47. Calcd. for $C_{26}H_{22}Br_2CuN_2O_2$ (brown): C, 50.50; H, 3.56; N, 4.53.

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 nujol mulls on KCl or KBr pellets as support (4000–400 cm^{-1}), and nujol mulls on polythene as support (600–100 cm^{-1}), were recorded on a Perkin-Elmer 180 spectrophotometer. The room temperature magnetic moments were measured by the Gouy method using $Ni(en)_3S_2O_3$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants. The e.p.r. spectra of polycrystalline samples were recorded on a JEOL PE-3X spectrometer. The spectra were calibrated with diphenylpicrylhydrazyl (DPPH, g = 2.0036) as a field marker.

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X-Ray Data Collection

The crystal selected for X-ray analysis was sealed into a glass capillary and was mounted on a Siemens AED automated four-circle diffractometer. All the measurements were carried out at room temperature, by using Ni-filtered Cu-Kα radiation, under the conditions listed in Table I. All data were corrected for Lorentz and polarization effects, but not for absorption in view of the small and almost isotropic crystal dimensions. Only the observed reflections, placed on an (approximately) absolute scale by means of a Wilson plot, were used in the structure determination.

Solution and Refinement of the Structure

The centrosymmetric space group P$\bar{1}$ was initially assumed and then confirmed by the subsequent refinement of the structure, which was solved by conventional Patterson and Fourier techniques. Full-matrix least-squares refinement [14] of positional and anisotropic thermal parameters for all the non-hydrogen atoms, and with the hydrogen atoms at ideal positions relative to their bonded atoms, led to final convergence at $R = 3.41\%$ and $R_w = 3.98\%$. The weighting scheme, automatically optimized by the program, was $w = 1.0/[\sigma^2(F) + 0.0029\ F_0^2]$. In the final least-squares cycle the shift of all parameters was less than 0.1 of an estimated standard deviation. The highest featureless peak in the last difference Fourier map was of. 0.27 e/Å^3. Complex neutral atom scattering factors [15] were used throughout; major calculations were carried out on a CDC Cyber 7600 computer by using the SHELX 76 program package [16] and the ORTEP plotting program [17]. The final positional parameters for non-hydrogen atoms are given in Table II. Lists of anisotropic temperature factors, of hydrogen atom parameters, and of observed and calculated structure factors are available [18].

TABLE I. Summary of Crystal Data Collection[a] for $CuCl_2L_2$.

Diffractometer	Siemens AED
Radiation	Ni-filtered Cu-Kα (λ = 1.54178 Å)
Temperature, °C	20 ± 2
Crystal system	triclinic
Space group	P$\bar{1}$ (C_i^1, No. 2)
a, Å	13.397(3)
b, Å	10.752(2)
c, Å	9.205(2)
α, degrees	72.26(1)
β, degrees	91.58(1)
γ, degrees	106.86(1)
V, Å^3	1206.02
Molecular weight	528.91
Z	2
F(000)	542
ρ(calcd), g/cm^3	1.46
ρ(obsd), g/cm^3	1.48 (by flotation in $CHCl_3$)
Reflections measd.	±h, ±k, ±l
Scan type	$\omega-2\vartheta$
ϑ range, degrees	2–70
Lowest scan speed	2.5°/min
Scan width max	1.1°
Standards	1 every 50 reflections (no changes)
Collected reflections	3238
Observed reflections	2581 with $I > 2.0\sigma(I)$ [$\sigma^2(I)$ = (total counts) + $(0.01 \times \text{intens})^2$]
Crystal size, mm	~0.15 × 0.15 × 0.21
μ(CuKα), cm^{-1}	33.5
Absorption corr.	not applied

[a] Unit cell parameters and their esd's were derived from least-squares fit to the setting angles of 25 strong reflections from diverse regions of reciprocal space.

Analyses

Nitrogen, carbon and hydrogen were analyzed with a C. Erba Elemental Analyser 1106.

TABLE II. Final Positional Parameters with Esd's in Parentheses for $CuCl_2L_2$.

Atom	x	y	z
Cu	0.4322(1)	0.2366(1)	0.4814(1)
Cl(1)	0.4206(1)	0.4445(1)	0.3285(1)
Cl(2)	0.3459(1)	0.0087(1)	0.5500(2)
N(1)	0.3734(2)	0.2782(3)	0.6558(4)
C(1)	0.3472(3)	0.1765(4)	0.8044(5)
C(2)	0.4262(4)	0.1619(5)	0.9009(6)
C(3)	0.4037(6)	0.0677(6)	1.0459(6)
C(4)	0.3017(7)	−0.0092(6)	1.0952(7)
C(5)	0.2242(5)	0.0003(5)	0.9964(7)
C(6)	0.2445(4)	0.0917(4)	0.8473(5)
C(7)	0.1592(4)	0.1006(5)	0.7427(6)
O(1)	0.1575(3)	0.2099(3)	0.6514(5)
C(8)	0.0732(4)	−0.0264(5)	0.7457(6)
C(9)	−0.0242(4)	−0.0154(6)	0.7021(8)
C(10)	−0.1036(5)	−0.1287(7)	0.6939(8)
C(11)	−0.0850(5)	−0.2547(6)	0.7302(7)
C(12)	0.0102(5)	−0.2680(5)	0.7737(7)
C(13)	0.0916(4)	−0.1542(5)	0.7827(6)
N(2)	0.5194(4)	0.2157(3)	0.3198(4)
C(14)	0.6066(3)	0.3356(4)	0.2542(5)
C(15)	0.6107(4)	0.4073(5)	0.0998(5)
C(16)	0.6912(4)	0.5265(5)	0.0360(5)
C(17)	0.7683(4)	0.5748(5)	0.1260(5)
C(18)	0.7642(3)	0.5026(4)	0.2801(5)
C(19)	0.6835(3)	0.3832(4)	0.3467(5)
C(20)	0.6737(3)	0.3210(4)	0.5161(5)
O(2)	0.5879(2)	0.2615(3)	0.5869(3)
C(21)	0.7693(3)	0.3378(4)	0.6035(5)
C(22)	0.7639(3)	0.3621(4)	0.7432(5)
C(23)	0.8507(4)	0.3723(5)	0.8297(6)
C(24)	0.9403(4)	0.3551(5)	0.7791(7)
C(25)	0.9457(4)	0.3301(5)	0.6413(7)
C(26)	0.8608(3)	0.3226(5)	0.5517(6)

TABLE III. Selected Interatomic Distances and Angles.

a) Distances (Å)			
Cu–Cl(1)	2.297(1)	Cu–Cl(2)	2.278(1)
Cu–N(1)	2.028(3)	Cu–N(2)	2.020(4)
Cu–O(2)	2.256(3)		
N(1)–C(1)	1.443(5)	N(2)–C(14)	1.443(5)
C(6)–C(7)	1.479(7)	C(19)–C(20)	1.490(6)
C(7)–O(1)	1.225(6)	C(20)–O(2)	1.232(5)
C(7)–C(8)	1.503(6)	C(20)–C(21)	1.489(5)
N(1)···O(1)	2.772(7)	H(2N1)···O(1)	1.99
N(1)···Cl(1$^{\text{i}}$)	3.463(4)	H(1N1)···Cl(1$^{\text{i}}$)	2.53
N(2)···Cl(2$^{\text{ii}}$)	3.340(4)	H(1N2)···Cl(2$^{\text{ii}}$)	2.41
b) Angles (deg)			
Cl(1)–Cu–Cl(2)	141.7(1)	Cl(1)–Cu–O(2)	110.3(1)
Cl(2)–Cu–O(2)	107.7(1)	N(1)–Cu–Cl(1)	86.6(1)
N(1)–Cu–Cl(2)	97.8(1)	N(1)–Cu–O(2)	89.8(1)
N(2)–Cu–Cl(1)	92.9(1)	N(2)–Cu–Cl(2)	89.8(1)
N(2)–Cu–O(2)	79.3(1)	N(1)–Cu–N(2)	168.2(1)
Cu–N(1)–C(2)	120.3(2)	Cu–N(2)–C(14)	113.0(2)
Cu–O(2)–C(20)	125.3(3)		
N(1)–C(1)–C(2)	118.4(4)	N(2)–C(14)–C(15)	119.3(4)
N(1)–C(1)–C(6)	120.7(4)	N(2)–C(14)–C(19)	120.3(4)
C(1)–C(6)–C(7)	121.9(4)	C(14)–C(19)–C(20)	121.8(4)
C(5)–C(6)–C(7)	120.7(5)	C(18)–C(19)–C(20)	119.2(4)
C(6)–C(7)–O(1)	121.3(4)	C(19)–C(20)–O(2)	121.6(4)
C(8)–C(7)–O(1)	118.7(5)	C(21)–C(20)–O(2)	118.9(4)
C(6)–C(7)–C(8)	120.0(4)	C(19)–C(20)–C(21)	119.5(4)
C(7)–C(8)–C(9)	119.1(5)	C(20)–C(21)–C(22)	118.4(4)
C(7)–C(8)–C(13)	121.3(5)	C(20)C(21)–C(26)	121.1(4)
N(1)–H(2N1)···O(1)	138.0	N(1)–H(1N1)···Cl(1$^{\text{i}}$)	169.0
N(2)–H(1N2)···Cl(2$^{\text{ii}}$)	165.3		

Superscripts refer to the following transformations of the reference coordinates: (i) 1 – x, 1 – y, 1 – z; (ii) 1 – x, –y, 1 – z.

TABLE IV. Magnetic, Electronic and Infrared Results for the Ligand, Its Hydrochloride Salt, the Complexes and Their Deuterated Analogues (in Parentheses) in the Solid State.

	L	L·HCl	$CuCl_2L_2$	$CuBr_2L_2$
μ_{eff}, μ_B			1.90	1.92
$g_\parallel$			2.024	2.062
$g_\perp$			2.109	2.150
			2.237	
d–d bands, 10^{-3} cm^{-1}			10.0sh	11.6
			13.0	14.6sh
C.T. bands, 10^{-3} cm^{-1}			21.5sh	20.8sh
			27.6	26.9
$\nu(NH_2)$, cm^{-1}	3440s(2575s)	2940vsb(2180sb)	3345m(2492s)	3350s
	(2520w)		3310m(2492s)	
	3320s(2480vw)	2550s(2060sb)	3278m(2450s)	3275s
	(2415s)		3170wb(2320s)	3170m
			3095m(2295m)	3090s
$\nu(CO)$, cm^{-1}	1625vs(1620vs)	1662vs(1660vs)	1650vs(1642s)	1650vs
			1630vs(1628vs)	1630vs
$\delta(NH_2)$, cm^{-1}	1575s*	1560s*	1608vs*	1610s*
		1518vs*	1562s*	1562s*
$\delta(NH_2)$, cm^{-1}		1140ms*	1090vs*	1100vs*
$\nu(Cu–X)$, cm^{-1}			282s(286s)	211vs

*These bands disappear on deuteration, reappearing at lower energies, in a spectral range in which, for the presence of ligand bands, they cannot be unambiguously assigned.

Results and Discussion

Description of the Structure

A drawing of the structure is shown in Fig. 1, along with the atom numbering. Selected interatomic distances and angles are reported in Table III. Lists of complete bond distances and bond angles are available [18].

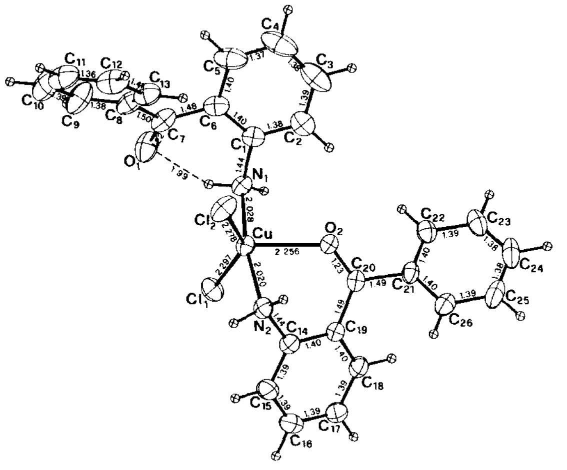

Fig. 1. ORTEP view of the $(2abf)_2CuCl_2$ complex showing the atom numbering, atomic vibrational ellipsoids (40%), and bond distances (Å). The hydrogen atoms are represented by spheres of arbitrary radius.

The structure consists of discrete $CuCl_2L_2$ monomers, interacting through weak hydrogen bonds. The coordination geometry about the copper ion involves a distorted trigonal bipyramidal stereochemistry, which is unusual for this type of complexes, most frequently showing square-pyramidal or elongated rhombic octahedral geometries [19]. The chlorines and the carbonyl oxygen from one ligand molecule are in the equatorial positions, while the two amino nitrogen atoms occupy the axial coordination sites.

The distortions from the ideal trigonal bipyramidal geometry appear to be mainly due to the balance of the repulsions among the three atoms in the equatorial plane ($\sphericalangle$Cl(1)–Cu–Cl(2) = 141.7(1)°), and to geometrical constraints by the ligand molecule acting as a bidentate one ($\sphericalangle$N(2)–Cu–O(2) = 79.3(1)°).

Similar distorted trigonal bipyramidal stereochemistries were previously observed for $[CuN_3X_2]$ (X = Cl, Br) chromophores [20]. A significant and surprising structural feature of the present complex is the shortening of the equatorial Cu–Cl bond distances (2.278(1) and 2.297(1) Å, respectively), when compared with the values found in regular (2.391(1) Å in $[Cr(NH_3)_6][CuCl_5]$ [21]) or distorted (from 2.364(2) to 2.421(2) Å in $[CuCl_2(1,2\text{-dimethylimidazole})_3]$ [22]) trigonal bipyramidal coordination geometries. Another relevant structural feature is the elongation of the equatorial Cu–O bond (2.256(3) Å); a similar effect was previously observed for equatorially bonded N atoms [20, 22, 23]. Axial Cu–N bond lengths are normal [19, 20, 22, 23].

All bond distances and bond angles within the ligand molecules are in the expected range and compare well with those reported for the free benzophenone molecule [24, 25].

The only significant difference between their dimensions involves the dihedral angle between the carbonyl group and the substituted benzene ring, which only in the bidentate L molecule is suitable for a strong intramolecular H-bond interaction between the carbonyl oxygen and one aminic proton (see Table III).

The crystal packing is mainly determined by intermolecular N–H···Cl interactions (see Table III). Their interatomic separations are consistent with weak hydrogen bonds [26].

Physical Results

Both complexes present a 'normal' room temperature magnetic moment for an orbitally non-degenerate ground state.

The polycrystalline EPR spectrum of the chloride complex (Table IV) is of a 'reversed' type, as usually observed for copper(II) in trigonal bipyramidal environments, with $g_\parallel$ lower than $g_\perp$ [19, 27]. In particular this latter is split, showing a distortion from D_{3h} symmetry, as shown by the structural results [19, 27, 28]. Therefore the two bands appearing in its electronic spectrum may be assignable as the split components of the transition d_{xy}, $d_{x^2-y^2} \rightarrow d_{z^2}$ ($^2A' \rightarrow {}^2E'$) [28, 29].

The more relevant IR bands (Table IV) are unambiguously assigned by comparing the spectra of the ligand, its hydrochloride salt, the complexes and their deuterated analogues. The splitings of NH_2 and CO bands in the complexes are consistent with the presence of two differently bonded ligand molecules. In particular the two CO stretching vibrations at 1650 and 1630 cm^{-1} may be reasonably assigned to uncoordinated C(7)–O(1) (1.225(6) Å) and coordinated C(20)–O(7) (1.232(5) Å), respectively.

It is also interesting to note that the infrared evidence of the CO coordination may be inferred only by comparison of the spectra of the complexes with that of the hydrochloride salt of the ligand, and not with that of the ligand, as is usually done. In the free ligand strong inter and intramolecular hydrogen interactions may explain the low CO frequency value.

In the far-IR spectra of the complexes two Cu–N, two Cu–X and one Cu–O stretching vibration are expected on the basis of an idealized C_{2v} symmetry. In view of the uncertainty in the assignment of Cu–N and Cu–O bands, only Cu–X frequencies are reported in Table IV.

Similar structures for both our complexes may be proposed on the basis of the strict similarity of their IR spectra. In particular, EPR and electronic spectra of the bromide complex (Table IV) suggest a lower distorted D_{3h} symmetry than in the chloride one.

Supplementary Material

Tables of calculated positional and thermal parameters for the hydrogen atoms, anisotropic thermal parameters, bond distances and bond angles within phenyl rings and selected least-squares planes are available from the Editor.

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