Benzophenoneimine Complexes of Copper(I)[☆]

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The reactions of $[(MeCN)_4Cu]BF_4$ with two or three equivalents of benzophenoneimine lead to the formation of $[(Ph_2C{=}NH)_2Cu]BF_4$ (**1**) and $[(Ph_2C{=}NH)_3Cu]BF_4$ (**2**), respectively. A further equivalent of the ligand does not coordinate to the cation of complex **2**. The crystal structures of both compounds were determined. **1** shows a linearly two-coordinated copper(I) center with a Cu–N distance of 1.877(2) Å. In compound **2** a distorted trigonal planar coordination of copper is observed with N–Cu–N angles of 114.5(2), 112.9(2) and 132.4(2)°, corresponding to two nearly equal Cu–N distances [Cu–N2 1.947(5) and Cu–N3 1.934(5) Å] and a significantly longer third one [Cu–N1 2.011(5) Å]. A comparison of these data with recently determined structures of bis(benzophenoneimine)silver(I) and -gold(I) complexes shows that the covalent radii of the monovalent coinage metals decrease in the order Ag(I) > Au(I) > Cu(I).

Introduction

Copper salts are used in the oxidative coupling of ammonia to produce hydrazine via ketimine intermediates[1–4]. The mechanism proposed for the action of the copper salts in both the stoichiometric and catalytic versions of this reaction includes the formation of ketimine complexes, but none of these intermediates has been isolated and structurally characterized.

In an attempt to contribute to this topic, a study was initiated focussing initially on the coordination chemistry of ketimines with gold(I) and silver(I)[5]. These investigations provided the first information on the stoichiometry, structure and properties of such complexes. In the course of the structural work we were intrigued by the findings regarding the covalent radii of gold(I) and silver(I) in their complexes with nitrogen donors, corroborating recent results for phosphane complexes[6]. For bis(benzophenoneimine)silver(I) and -gold(I) tetrafluoroborates, the cations are nearly superimposable except for the different metal–nitrogen distances, which are found to be $r(Ag^+) > r(Au^+)$.

In order to extend these studies of the radii of the coinage metals to isostructural copper(I) complexes, we have now prepared and structurally characterized two benzophenoneimine complexes of copper(I).

Preparative Results

The reaction of $[(MeCN)_4Cu]BF_4$ with two equivalents of benzophenoneimine give a high yield of the pale yellow complex $[(Ph_2C{=}NH)_2Cu]BF_4$ (**1**), with a melting point of 219°C (eq. 1).

$$[(MeCN)_4Cu]BF_4 + 2(3)\ Ph_2C{=}NH \longrightarrow \underset{\mathbf{1(2)}}{[(Ph_2C{=}NH)_{2(3)}Cu]BF_4} + 4\ MeCN \qquad (1)$$

Analytical and spectroscopic data are in full agreement with the proposed formula. In the NMR spectra, in $CDCl_3$ at 25°C, the proton resonances are broad and it is only at low temperature (–60°C) that sharp resonances are obtained including the proton signal of the NH group.

The analogous 2:1 complexes of silver(I) and gold(I) were found to be inert towards a further equivalent of benzophenoneimine. By contrast, treatment of the copper(I) complex **1** with a third molecule of the ketimine leads to a complete transformation of the substrate into an orange complex $[(Ph_2C{=}NH)_3Cu]BF_4$ (**2**). Addition of a fourth molecule of the imine is not observed, however. Analytical data of crystals of **2**, obtained from a tetrahydrofuran/pentane mixture, show the product to contain one solvent molecule (thf), but according to the single crystal X-ray studies (see below) this solvent molecule is not coordinated to the copper(I) center.

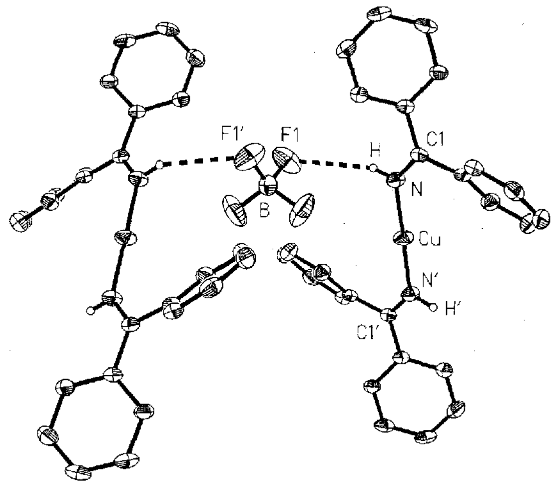
The NMR spectra of complex **2** show only one set of signals for the three $Ph_2C{=}NH$ ligands, even at –60°C. This indicates structural equivalence of the ligands or an extremely rapid site exchange in a nonsymmetrical structure. The FAB mass spectrum of **2** shows only the 2:1 complex cation $[(Ph_2C{=}NH)_2Cu]^+$, which is obviously generated by loss of one imine ligand.

In the solid state compounds **1** and **2** are air-stable, but in solution (in the air) rapid oxidation to a green unidentified material is observed.

Molecular Structures of the Complexes 1 and 2

Crystals of $[(Ph_2C{=}NH)_2Cu]^+BF_4^-$ (**1**) are monoclinic, space group *C2/c*, with $Z = 4$ formula units in the unit cell. The lattice consists of tetrafluoroborate anions and bis(ketimine)copper(I) cations. The copper(I) atom lies at a center of inversion relating the two ligands of the cation by symmetry. The geometry of the cation (point group C_i) is very similar to that found for the corresponding silver(I) and gold(I) complexes, which crystallize in space groups *C2/c* and $P2_1/c$ and have point group C_i, or close to C_i, respectively, for the cations[5]. The tetrafluoroborate anions of **1** are engaged in weak hydrogen bonding to the N–H groups of two cations via two of the four fluorine atoms (F1–H 2.667 Å, N–H 0.834 Å, N···F1 3.417 Å and N–H···F1 150.2°). By symmetry the N–Cu–N′ unit is linear, with two identical Cu–N bonds [1.877(2) Å]. This value is not unusual and lies in the range of distances (1.85–1.89 Å) found in other linearly two-coordinated imine–copper(I) complexes[7–15]. These complexes include a variety of N-bonded Schiff bases, oxazolines, triazoles, pyrazoles, benzimidazoles, pyridines, acetamidines, benzothiadiazoles and benzopyrimidines.

Figure 1. Crystal structure of $[(Ph_2C{=}NH)_2Cu]^+$ BF_4^- (**1**). Two cations and one tetrafluoroborate anion are shown (ORTEP plot, 50% probability ellipsoids; phenyl hydrogen atoms are omitted). Selected bond lengths (Å) and angles (°): Cu–N 1.877(2), N–C1 1.287(2), N–H 0.83(2), N–Cu–N′ 180.0, C1–N–Cu 131.84(13), Cu–N–H 113(2)



Crystals of tris(benzophenoneimine)copper(I) tetrafluoroborate ($2 \cdot C_4H_8O$), obtained by cautiously layering a thf solution with pentane, are monoclinic, space group $P2_1/n$, with $Z = 4$ formula units in the unit cell. The lattice is composed of $[(Ph_2C{=}NH)_3Cu]^+$ cations, BF_4^- anions and one solvent molecule thf, which is not easily released even in a vacuum. The copper atom is in a planar threefold configuration with the three ketimine ligands, with one unusually long and two short Cu–N distances [Cu–N1 2.011(5), Cu–N2 1.947(5) and Cu–N3 1.934(5) Å] associated with one much larger angle [N2–Cu–N3 132.4(2)°] and two smaller angles [N1–Cu–N2 114.5(2) and N1–Cu–N3 112.9(2)°]. Rather than describing it as trigonal planar, the cation can also be regarded as a distorted linear two-coordinate Cu(I) complex, which is "affected" structurally by a third ligand of the same type. It should be noted that the two short Cu–N bonds in **2** are only slightly longer than in **1**, whereas the remaining one (Cu–N1 in **2**) is grossly extended. The average Cu–N distance in **2** (1.964 Å) is about 5% greater than the average in **1** (1.877 Å), as expected for a species with an increased coordination number.

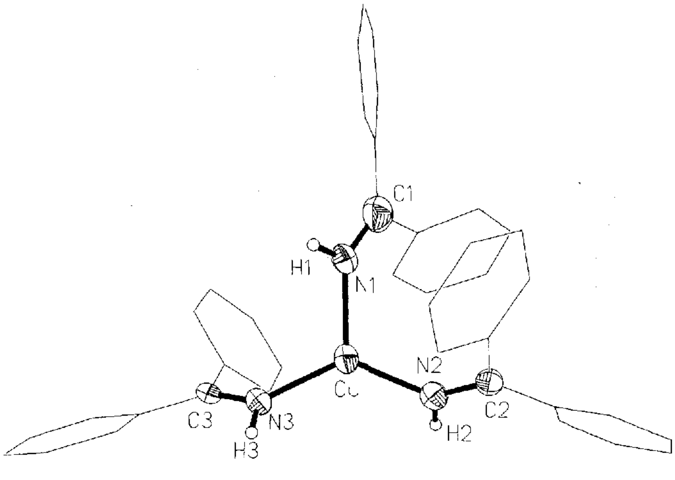
In the literature three types of structures are known for three-coordinated imine–copper(I) complexes: symmetrical

Table 1. Crystallographic data for $[(Ph_2C{=}NH)_2Cu]^+BF_4^-$ (**1**) and $[(Ph_2C{=}NH)_3Cu]^+BF_4^- \cdot$ thf (**2**·thf)

Compound	**1**	**2**·thf
empirical formula	$C_{26}H_{22}BCuF_4N_2$	$C_{43}H_{41}BCuF_4N_3O$
formula weight	512.81	766.14
crystal system	monoclinic	monoclinic
space group (No.)	*C2/c* (No. 15)	$P2_1/n$ (No. 14)
a [Å]	18.194(1)	14.012(2)
b [Å]	7.571(1)	13.044(2)
c [Å]	17.075(1)	20.794(3)
α [°]	90	90
β [°]	103.51(1)	98.07(1)
γ [°]	90	90
V [Å^3]	2286.9(4)	3762.9(10)
ρ_{calc} [gcm^{-3}]	1.489	1.352
Z	4	4
F(000) [e]	1048	1592
μ(Mo-K_α) [cm^{-1}]	10.0	6.4
T [°C]	–74	–62
diffractometer	Enraf Nonius CAD4	Enraf Nonius CAD4
scan	ω-θ	θ-θ
hkl range	$-22 \le h \le 23, 0 \le k \le 9, -21 \le l \le 1$	$-16 \le h \le 16, 0 \le k \le 15, 0 \le l \le 24$
measured reflections	2731	5025
unique reflections	2494	5007
used reflections	2492	4990
R_{int}	0.0086	0.0186
refined parameters	200	490
H atoms (found/calc.)	22 / –	– / 24
absorption corr.:	none	empirical
T_{min} / T_{max}		0.9301 / 0.9993
$R1^{[a]}$ [$F_o \ge 4\sigma(F_o)$]	0.0345	0.0690
$wR2^{[a]}$ (used refl.)	0.0934	0.1736
weighting scheme[a]	$a = 0.0618, b = 1.8181$	$a = 0.1019, b = 5.3998$
ρ_{fin}(max/min) [eÅ^{-3}]	+0.673 / –0.446	+0.848 / –0.385

[a] $R1 = \Sigma(||F_o|-|F_c||)/\Sigma|F_o - wR2 = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$. – $w = q/2\sigma^2(F_o^2) + (ap)^2 + bp, p = (F_o^2 + 2F_c^2)/3$.

Figure 2. Crystal structure of the cation $[(Ph_2C{=}NH)_3Cu]^+$ in **2** (ORTEP plot, 50% probability ellipsoids, except for arene carbon atoms; arene hydrogen atoms are omitted). Selected bond lengths (Å) and angles (°): Cu–N1 2.011(5), Cu–N2 1.947(5), Cu–N3 1.934(5), N1–C1 1.250(9), N2–C2 1.286(8), N3–C3 1.295(8), N1–Cu–N2 114.5(2), N1–Cu–N3 112.9(2), N2–Cu–N3 132.4(2), C1–N1–H1 115.0(5), C2–N2–H2 116.5(4), C3–N3–H3 114.9(3), C1–N1–Cu 130.7(5), C2–N2–Cu 126.7(5), C3–N3–Cu 129.7(4)



in [tris(monoazadiene)copper(I)] triflate [all N–Cu 1.999(5) Å and N–Cu–N 120°][16], distorted trigonal in a (triazolyl)copper(I) complex [Cu–N1 1.95(3) Å, Cu–N2 2.10(3) Å, Cu–N3 1.97(3) Å, N1–Cu–N2 93.007°, N2–Cu–N3 124.912° and N1–Cu–N3 135.322°][15] and distorted trigonal planar in a tris(oxazoline)copper(I) complex [Cu–N1 1.957(3) Å, Cu–N2 2.122(3) Å, Cu–N3 1.948(3) Å, N1–Cu–N2 108.05(13)°, N2–Cu–N3 105.17(13)° and N1–Cu–N3 146.26(13)°][17].

Discussion and Conclusions

The present work has shown that simple ketimines $R_2C=NH$, the basic members of the Schiff base series bearing only hydrogen at the imine function, are good unidentate ligands for univalent copper. Addition is facile up to a coordination number of 2, associated with a linear coordination geometry (compound **1**). A third equivalent of the ligand is accepted only reluctantly, and the product shows inequivalent bonding of the three ligands. The coordination geometry of compound **2** is still reminiscent of the linear two-coordination, with one particularly large N–Cu–N angle. With this result in mind, it is not surprising that a fourth ligand molecule cannot be accommodated at the copper(I) center, even if an innocent counterion like BF_4^- is the only potential competitor and an excess of ligand is applied in a polar solvent.

Because the cation of compound **2** does not have standard trigonal geometry, an evaluation of its geometrical details in terms of bonding characteristics may not be very meaningful. However, compound **1** does have such a standard structure, and therefore comparisons can be made with data from reference compounds of the other two coinage metals.

A superposition of the cation structures (Figure 3) of the three tetrafluoroborate salts $\{[(Ph_2C=NH)_2M]^+[BF_4]^-\}$, M = Cu, Ag, Au, shows a good general agreement of the configurations, although different types of hydrogen bonding between cations and anions lead to concomitant variations in conformational details.

It is obvious, however, that the difference in the radii of the metal cations is the most significant variation on going through the coinage metal series. Silver(I) is found to be by far the largest of the three congeners, followed by gold(I), and finally by copper(I) (Table 2, Figure 3). This result is in excellent agreement with a recent revision of the tabulated radii of the coinage metals, which also ties up with theoretical calculations considering relativistic and correlation effects[6].

It therefore appears that there is now general agreement of the data, when they are carefully chosen from groups of compounds with comparable stoichiometries and structures.

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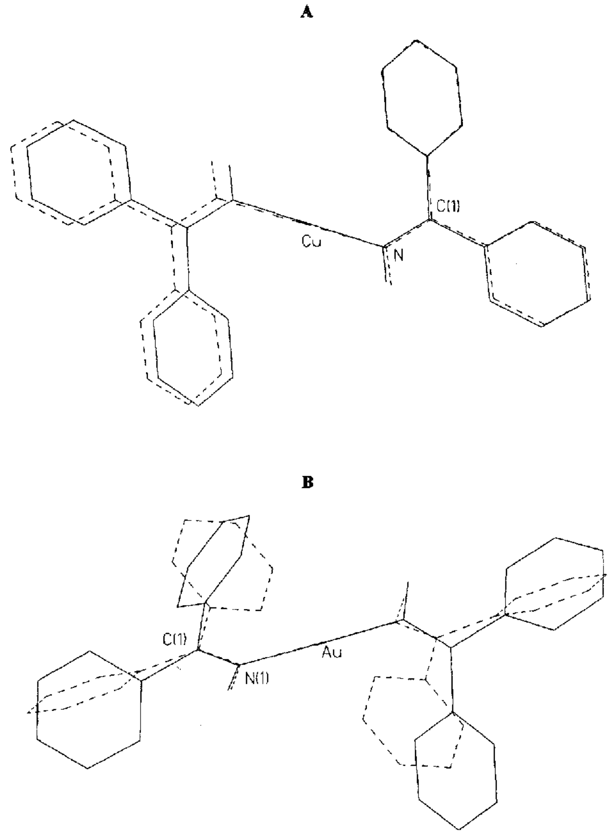

Figure 3. A: Superposition of the bis(benzophenoneimine)silver(I) (dotted line) and -copper(I) (continuous line) complexes: Ag–N 2.113(2); B: Superposition of the bis(ketimine)copper(I) (dotted line) and -gold(I) (continuous line) complexes: Au–N 1.999 Å (average)

Table 2. Nitrogen–metal distances in $[(Ph_2C=NH)_2M]^+$ cations [M = Cu(I), Ag(I) and Au(I)]

Compound	M–N bond distance in Å
$[(Ph_2C=NH)_2Cu]^+BF_4^-$	1.877(2)
$[(Ph_2C=NH)_2Ag]^+BF_4^-$[5]	2.113(2)
$[(Ph_2C=NH)_2Au]^+BF_4^-$[5]	1.999(4) and 1.998(4)

Experimental Section

All experiments were carried out under an atmosphere of dry, purified nitrogen. Glassware was dried and filled with nitrogen; solvents were distilled and kept under nitrogen. – NMR: Jeol GX 400, TMS as internal standard. – MS: Finnigan MAT 90. – Microanalyses: In-house analyzers (by combustion and atomic absorption spectroscopy). – Starting materials were either commercially available or were prepared following literature procedures: $Ph_2C=NH$[18], $[(MeCN)_4Cu]BF_4$[19].

Bis(benzophenoneimine)copper(I) Tetrafluoroborate (**1**): To a solution of benzophenoneimine (93 µl, 0.55 mmol) in tetrahydrofuran (10 ml) was added slowly a solution of $[(MeCN)_4Cu]BF_4$ (0.87 g, 0.275 mmol) in tetrahydrofuran (10 ml) at room temperature. The solution immediately turned orange, but after a few seconds it became colourless. After 30 min the solvent was removed under vacuum and the pale yellow residue was taken up in dichloromethane, filtered, and the filtrate layered with pentane. After several days pale yellow crystals of bis(benzophenoneimine)gold(I) tetrafluoroborate were obtained. – Yield 0.135 g (96%), m.p.

219°C. – ^1H NMR ($CDCl_3$, −60°C): $\delta = 9.27$ [br. s, 1H, NH], 7.30–7.49 [m, 10H, Ph]. – $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temp.): $\delta = 137.2$ [br., *ipso*-C]; 131.5 [br., *para*-C], 128.2–129.8 [br., *ortho*- and *meta*-C], [C=N] was not observed. – $C_{26}H_{22}CuBF_4N_2$ (512.81): calcd. C 60.90, H 4.32, N 5.46; found C 60.90, H 4.51, N 5.47. – MS (FAB); *m/z* (%): 424.9 $[(Ph_2C{=}NH)_2Au]^+$ (100), 243.9 $[(Ph_2C{=}NH)Cu]^+$ (40.2).

Tris(benzophenoneimine)copper(I) Tetrafluoroborate (**2** • thf): To a solution of $[(MeCN)_4Cu]BF_4$ (0.10 g, 0.32 mmol) in tetrahydrofuran (15 ml), benzophenoneimine (168 µl, 1.00 mmol) was added at room temperature. Immediately the solution turned orange. After 30 min of stirring the solution was filtered and cautiously layered with pentane. Orange crystals were obtained after 2 d. Yield 0.20 g (81%), m.p. 105°C. – ^1H NMR ($CDCl_3$, room temp.): $\delta = 9.25$ [br. s, 1H, NH], 7.37–7.57 [m, 10H, Ph–H], 3.73 [m, 4H, CH_2O], 1.81 [m, 4H, CH_2]. – $^{13}C\{^1H\}$ ($CDCl_3$, −60°C): $\delta = 175.7$ [s, C=N], 137.1 and 136.9 [s, *ipso*-C], 131.2 [br., *para*-C], 128.0–128.9 [br., *ortho*- and *meta*-C]. – $C_{43}H_{41}CuBF_4N_3O$ (766.14): calcd. C 67.41, H 5.39, N 5.47, Cu 8.60; found C 67.42, H 5.40, N 5.48, Cu 8.30. – MS (FAB); *m/z* (%): 425.2 $[(Ph_2C{=}NH)_2Cu]^+$ (100), 244.2 $[(Ph_2C{=}NH)Cu]^+$ (77).

Crystal Structure Determination: Suitable crystals of compounds **1** and **2** were sealed into glass capillaries and used for measurement of precise cell constants and collection of intensity data. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for either compound. Diffraction intensities were corrected for Lp and absorption effects. The structures were solved by direct methods and refined by full matrix least squares calculations against F^2[20]. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in idealized positions and allowed to ride on their corresponding carbon or nitrogen atoms. Their isotropic thermal parameters were tied to that of the adjacent atom by a factor of 1.5. Selected interatomic distances and angles are given in the figure captions. Crystal and structure solution data are summarized in Table 1. Further information may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository numbers CSD-406580 (**1**) and -406581 (**2**), the names of the authors, and the journal citation.

☆ Dedicated to Professor *J. Strähle* on the occasion of his 60th birthday.

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