A Novel Triangular Trinuclear μ_3-CO_3 Ferromagnetic Cu^{II} Compound Prepared in situ from CO_2 Uptake in Air. X-ray Structure, Spectroscopy and Magnetism

Gerard A. van Albada,[a] Ilpo Mutikainen,[b] Olivier S. Roubeau,[a] Urho Turpeinen,[b] and Jan Reedijk*[a]

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The new trinuclear compound $[Cu_3(bpy)_6(\mu_3\text{-}CO_3)](BF_4)_4(H_2O)_2(C_2H_6O)$ (in which bpy = 2,2′-bipyridine) has been synthesized from $Cu(BF_4)_2$ and bpy in aqueous ethanol by rapid uptake of atmospheric CO_2. The structure of the compound has been determined by X-ray crystallography; it was found to crystallise in the triclinic space group $P\bar{1}$ with a = 13.405(7), b = 13.691(7), c = 21.446(8) Å, α = 82.87(4), β = 73.57(4), γ = 64.32(4)°, Z = 2. The three copper atoms are connected to each other through the oxygen atoms from the bridging carbonato group, giving a triangular array of copper atoms. Each copper has a distorted square-pyramidal environment with a basal plane formed by three nitrogen atoms of the two chelating bipyridine groups and the oxygen atom of the bridging carbonato group (Cu–N/O distances about 2.0 Å). The apical position is formed at each copper by the fourth nitrogen atom of the bipyridines with distances varying from 2.120(5) to 2.188(5) Å. A weak ferromagnetic interaction is observed between the copper(II) ions. All data were fitted using the Hamiltonian $H = -J_{12}(\mathbf{S}_1\cdot\mathbf{S}_2) - J_{13}(\mathbf{S}_1\cdot\mathbf{S}_3) - J_{23}(\mathbf{S}_2\cdot\mathbf{S}_3)$. Observed parameters are J = 10.6 cm^{-1} and a very weak antiferromagnetic intercluster interaction with zj' = −1.2 cm^{-1}.

Introduction

Over the years many efforts have been made in the search for compounds that can act as a CO_2 catcher, i.e. insertion of CO_2 from the atmosphere into coordination compounds. Insertion reactions of CO_2, such as into metal−ligand bonds, are not uncommon and in recent years many review papers have been published on this subject.[1] Several dinuclear copper(II) compounds have been synthesized by means of fixation of CO_2 from air.[2] The carbonate anion itself is a versatile bridging ligand, which can bind in different modes to generate dinuclear, trinuclear, tetranuclear, and even one- or two-dimensional systems,[3] and the study of this subject is also important in relation to the zinc(II) compounds in carbonic anhydrases (CA).[4]

Absorption of CO_2 into a trinuclear copper(II) compound was suggested in 1968 on the basis of IR spectra,[10] but to the best of our knowledge only five crystal structures of this type of trinuclear copper(II) carbonato compound have been solved and published together with their magnetic properties.[4−9]

With the ligand 2,2-bipyridine (abbreviated as bpy), X-ray structures of dinuclear μ-hydroxo-bridged copper(II) coordination compounds with the general formula $[Cu(OH)(bpy)]_2(A)_x$ (x = 1,2 and A = ClO_4^-,[11] $CF_3SO_3^-$,[12] SO_4^{2-},[13] NO_3^-,[14a,14b] $C_4O_4^{2-}$ [14c] are known.

With perchlorate or nitrate as an anion, the X-ray structures of the mononuclear compounds with the general formula $Cu(bpy)_x(A)_2$ (x = 1−3) have been published.[14b,15] However, with tetrafluoroborate as an anion, only a mononuclear compound, $Cu(bpy)_2(BF_4)_2$, has been reported so far.[16] Following earlier research on dinuclear hydroxo and alkoxo-bridged copper(II) coordination compounds,[17] we attempted to synthesize the dinuclear hydroxo-bridged compound with the anion BF_4^- in the same way as for the other hydroxo-bridged compounds with bpy. However, in this case it was not the dinuclear hydroxo-bridged that was obtained, but surprisingly the trinuclear carbonato-bridged compound $[Cu_3(bpy)_6(\mu\text{-}CO_3)](BF_4)_4(H_2O)_2(C_2H_6O)$. It is remarkable that this compound has not been found earlier, considering the thorough research undertaken with the ligand bpy over many years. The title compound was subsequently easily synthesized in an artificial CO_2 atmosphere. With Zn^{II} and bpy as a ligand, the carbonato-bridged trinuclear compound $[Zn_3(bpy)_6(CO_3)(H_2O)](ClO_4)_4(bpy)\cdot 2H_2O$ is also known.[18] In this study we report the synthesis, spectroscopic and magnetic properties as well as the X-ray structure of the title compound.

[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
P.O. Box 9502, 2300 RA Leiden, Netherlands
E-mail: mailto:reedijk@chem.leidenuniv.nl
[b] Laboratory of Inorganic Chemistry, Department of Chemistry, University of Helsinki,
P.O. Box 55 (A.I.Virtasen aukio 1), 00014, Helsinki, Finland

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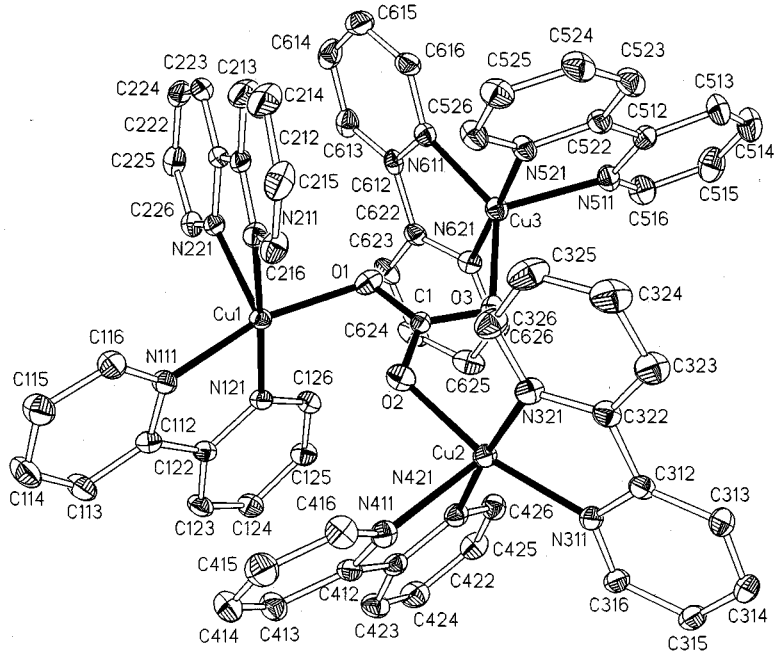

Figure 1. ORTEP plot showing the structure of $[Cu_3(bpy)_6(\mu\text{-}CO_3)](BF_4)_4(H_2O)_2(C_2H_6O)$ with atom-labeling scheme; hydrogen atoms, noncoordinating tetrafluoroborate anions, ethanol and water molecules are omitted for clarity

Results and Discussion

Description of the Crystal Structure of $[Cu_3(bpy)_6(\mu_3\text{-}CO_3)](BF_4)_4(H_2O)_2(C_2H_6O)$

The structure contains the unit $[Cu_3(bpy)_6(\mu_3\text{-}CO_3)]$, which is depicted in Figure 1, and the relevant bond length and bond angle information is given in Table 1. The unit cell also contains four noncoordinating tetrafluoroborate anions, one ethanol and two water molecules.

The three copper(II) atoms are connected to each other through the oxygen atoms from the bridging carbonato group, giving a triangular array of copper atoms. Each copper has a distorted square pyramidal environment with a basal plane formed by three nitrogen atoms of the two bichelating bipyridine groups and the oxygen atom of the bridging carbonato group (Cu−N/O distances about 2.0 Å). The apical position is formed at each copper by the fourth nitrogen atom of the bipyridines with distances that vary from 2.120(5) to 2.188(5) Å. The distortion from square pyramidal is different for each copper atom and this can be seen from the angles of each basal plane [Cu1 (basal plane O1−N211−N111−N121), angles 176.92(18) and 164.41(17)°; Cu2 (basal plane O2−N321−N311−N421), angles 172.8(2) and 166.76(17)°; Cu3 (basal plane O3−N521−N611−N621), angles 178.4(2) and 138.91(17)°]. This difference can be best expressed with the parameter τ (for 5 coordinated coordination compounds τ describes the relative amount of trigonality; τ = 0 for a square pyramid and τ = 1 for a trigonal bipyramid),[19] which has values of 0.21, 0.10 and 0.66 for Cu1, Cu2 and Cu3, respectively. The distances between the copper(II) atoms are also different and are large (Cu1−Cu2 4.64, Cu1−Cu3 4.72, Cu2−Cu3 5.00 Å).

The structures of compounds **1**−**4** in Table 2, in which the three coppers are almost equivalent, are quite different from that of compound **5**, in which all three copper atoms have a trigonal bipyrimidal geometry (τ values of 0.78, 0.81, and 0.83 for Cu1, Cu2, and Cu3, respectively).

The geometry in the related Zn compound, $[Zn_3(bpy)_6(\mu_3\text{-}CO_3)(H_2O)](ClO_4)_4(bpy)\cdot 2H_2O$,[18] is quite different; two of the Zn^{II} atoms have a distorted octahedral $N_4O(O_{water})$ geometry and the third Zn^{II} atom has a distorted trigonal-bipyramidal geometry with an N_4O environment.

Spectroscopy

The ligand field spectrum of the title compound shows a broad asymmetric band with a maximum at about $13.7\cdot 10^3$ cm^{-1} and a shoulder at about $10.1\cdot 10^3$ cm^{-1}; these absorptions are in agreement with a distorted square pyramidal $Cu(N)_x(O)_y$ geometry.[20]

In the infrared spectrum the most significant bands are those of the carbonato anion, which are reported in the literature at 1475, 1425, 837, 782, and 672 cm^{-1} for the compound $Cu_3(dpt)_3(\mu_3\text{-}CO_3)(ClO_4)_2\cdot 2H_2O$ (in which dpt = dipropylenetriamine)[10] and at 1476, 1423, 841, 694 cm^{-1} for the compound $[Zn_3(bpy)_6(\mu_3\text{-}CO_3)(H_2O)](ClO_4)_4(bpy)\cdot 2H_2O$.[18]

In the title compound the out-of-plane vibration at 839 cm^{-1} (medium intensity) is the best indication of the presence of CO_3 in the compound, as this spectral range is completely transparent in the monomeric compound $Cu(bpy)_3(BF_4)_2$.

EPR

The EPR spectrum of the title compound at room temperature shows a broad absorption centered around g =

Table 1. Bond lengths [Å] and angles [°]

Cu(1)−N(121)	1.983(4)
Cu(1)−N(211)	2.001(4)
Cu(1)−O(1)	2.022(4)
Cu(1)−N(111)	2.028(5)
Cu(1)−N(221)	2.156(5)
Cu(2)−O(2)	1.969(4)
Cu(2)−N(321)	1.987(5)
Cu(2)−N(421)	2.007(4)
Cu(2)−N(311)	2.040(4)
Cu(2)−N(411)	2.188(5)
Cu(3)−N(621)	1.974(5)
Cu(3)−N(521)	1.992(5)
Cu(3)−N(611)	2.055(5)
Cu(3)−O(3)	2.078(5)
Cu(3)−N(511)	2.120(5)
N(121)−Cu(1)−N(211)	176.92(18)
N(121)−Cu(1)−O(1)	94.76(17)
N(211)−Cu(1)−O(1)	88.03(18)
N(121)−Cu(1)−N(111)	80.64(18)
N(211)−Cu(1)−N(111)	96.34(19)
O(1)−Cu(1)−N(111)	164.41(17)
N(121)−Cu(1)−N(221)	102.30(17)
N(211)−Cu(1)−N(221)	78.95(18)
O(1)−Cu(1)−N(221)	90.35(16)
N(111)−Cu(1)−N(221)	105.16(18)
O(2)−Cu(2)−N(321)	94.46(18)
O(2)−Cu(2)−N(421)	89.20(17)
N(321)−Cu(2)−N(421)	172.8(2)
O(2)−Cu(2)−N(311)	166.76(17)
N(321)−Cu(2)−N(311)	80.53(19)
N(421)−Cu(2)−N(311)	94.55(18)
O(2)−Cu(2)−N(411)	85.92(18)
N(321)−Cu(2)−N(411)	107.28(19)
N(421)−Cu(2)−N(411)	79.16(19)
N(311)−Cu(2)−N(411)	107.24(18)
N(621)−Cu(3)−N(521)	178.4(2)
N(621)−Cu(3)−N(611)	80.0(2)
N(521)−Cu(3)−N(611)	98.3(2)
N(621)−Cu(3)−O(3)	91.28(18)
N(521)−Cu(3)−O(3)	89.90(18)
N(611)−Cu(3)−O(3)	138.91(17)
N(621)−Cu(3)−N(511)	101.3(2)
N(521)−Cu(3)−N(511)	79.3(2)
N(611)−Cu(3)−N(511)	109.90(18)
O(3)−Cu(3)−N(511)	111.19(17)

2.13 with a very weak shoulder at about $g = 2.42$. For the five other known trinuclear carbonato-bridged compounds the g values also lie at around $g = 2.12$ (see Table 2).

In frozen solution (DMF/methanol mixture) at 77 K a resolved $d_{x^2-y^2}$ spectrum is obtained with a $g_\perp$ value of 2.06, a $g_{//}$ of 2.26, with an $A_{//}$ value of 15.9 mT. A poorly resolved nitrogen hyperfine splitting is observed with 5 lines, indicating 2 nitrogens around the copper atom. This observation indicates that the compound is dissociated in this solution.

Magnetic Properties

To better understand the magnetic interaction, mediated through the CO_3^{2-} bridge, the magnetic susceptibilities of powdered samples were measured from 4 to 250 K and the results are shown in Figure 2 in the form of χ_m vs. T and μ_{eff} vs. T plots. The effective magnetic moment, μ_{eff}, measured from 250 to about 100 K has an almost constant value of about 3.3−3.4 μ_B. This value compares well with that expected for three uncoupled spins $S = {}^1/_2$ ($\mu_{eff} = 3.0\ \mu_B$, spin only value) and is also observed in other trinuclear triangular compounds.[4,21] Below 100 K the magnetic moment increases gradually until a maximum is reached at 5 K. The increase can be ascribed to a ferromagnetic interaction between the Cu^{II} ions.[4,7] The magnetic data were fitted to the theoretical expression for the magnetic susceptibility for a trinuclear triangular system, which is based on the general Hamiltonian[22,23] for the description of the interaction: $H = -J_{12}\ (\mathbf{S}_1 \cdot \mathbf{S}_2) - J_{13}\ (\mathbf{S}_1 \cdot \mathbf{S}_3) - J_{23}\ (\mathbf{S}_2 \cdot \mathbf{S}_3)$

in which the exchange integrals, J_{ij}, are negative for antiferromagnetic and positive for ferromagnetic interactions.

Although the three Cu^{II} ions are not completely identical (not related by a C_3 axis), we have assumed the Cu^{II} triangle to be equilateral. Considering three different Cu^{II} ions would only yield more ambiguous J_{ij} parameters, since they are strongly related to each other,[23a] and in our case without a better quality of fit. The g tensors and the J_{ij} parameters were therefore considered to be identical for the three Cu^{II} ions, and only one J value was considered.

The expression for the molar susceptibility then becomes:[22,23] $\chi_m = [Ng^2\mu_B^2/(4\ k_B\ (T + \Theta))] \times F$, where $\Theta = -(zJ'/k_B) \times F$

In this formula $F = [1 + 5\ \exp(3J/2kT)]/[1 + \exp(3J/2kT)]$ and the parameters N, g, μ_B, k_B, and T have their usual meanings.[22,23] The exchange parameter is denoted as J and the parameter zJ' empirically takes into account the intercluster interactions of z nearest neighbors.

Using the g value given by the EPR spectra and free variation of J did not give satisfactory results; therefore both J and g were left free in the least-squares fitting procedure, first considering $zJ' = 0$. Once the best fit was reached, the intercluster interaction was also introduced into the fitting procedure.

So, with variation of the three parameters J, zj', and g, and by minimizing the function $R = (\chi_m T_{calc} - \chi_m T_{obs})^2/(\chi_m T_{obs})^2$, the best fit was obtained for $J = 10.6\ cm^{-1}$, $zj' = -1.2\ cm^{-1}$, $g = 2.22$, and $R = 2.4 \cdot 10^{-4}$.

This low J value and rather weak interaction is not surprising since the distances between the copper(II) atoms are quite large (Cu−Cu separation of about 4.78 Å). As can be seen from Table 2, the present parameters agree well with the first four carbonato-bridged trinuclear compounds (compounds 1−4 in Table 2) reported in the literature. In fact, only compound **5** shows a very weak antiferromagnetic interaction,[9] the reasons for which are currently not understood.

Conclusion

In this paper a compound is described that is readily formed by absorption of CO_2 from the atmosphere, yielding a trinuclear carbonato-bridged compound having a $[Cu_3(bpy)_6(\mu_3\text{-}CO_3)]$ chromophore. The Cu^{II} ions are weakly coupled in a ferromagnetic manner, as also observed

Table 2. X-ray structure parameters and magnetism for Cu^{II} trinuclear μ_3-CO_3 compounds

Compound[a]	Coordination (chromophore)	Cu−X dist.(Å)	EPR (solid, RT)	Mag. susc. (cm^{-1})	ref.
1 $[Cu_3(pip)_3(H_2O)_3(\mu_3\text{-}CO_3)](NO_3)_4$	$CuN_3O(O_w)$	Cu−N,$O_{(av)}$ 2.00 Cu−O_w 2.25[b]	2.13	J = 9.64 zJ' = −0.079[c]	[5]
2 $[Cu_3(L)_3(\mu_3\text{-}CO_3)](ClO_4)_4$	$CuN_3O(O)$	Cu−N,$O_{(av)}$ 2.00 Cu−O 2.53	2.10 (br)	J = 8.2[d]	[4,6]
3 $[Cu_3(Medpt)_3(\mu_3\text{-}CO_3)](ClO_4)_4$	$CuN_3O(O_{ClO4})$	Cu−N,$O_{(av)}$ 2.00 Cu−$O_{(av)}$ 2.45	2.11	J = 12.6 zJ' = −0.68[e]	[7]
4 $[Cu_3(L2)_3(\mu_3\text{-}CO_3)](ClO_4)_4\cdot 2H_2O$	$CuN_3O(N)$	Cu−N,$O_{(av)}$ 2.00 Cu−N 2.10	[f]	J = 17.2[d]	[8]
5 $[Cu_3(TPA)_3(\mu_3\text{-}CO_3)](ClO_4)_4$	$CuN_3O(N)$	Cu−N,$O_{(av)}$ 2.04 Cu−$N_{(av)}$ 2.20	[f]	J = −1.19[d]	[9]
6 $[Cu_3(bpy)_6(\mu_3\text{-}CO_3)](BF_4)_4(H_2O)_2(C_2H_6O)$	$CuN_3O(N)$	Cu−N,$O_{(av)}$ 2.01 Cu−$N_{(av)}$ 2.15	$g_\perp$ 2.13 $g_{//}$ 2.42 (br,vw)	J = 10.6 zJ' = −1.2	this work

[a] Abbreviations: (v)w = (very)weak, br = broad, av = average value, O_w = O of water, RT = room temperature, av = average. − pip = 2-[2-(2-pyridyl)ethyliminomethyl]pyridine; L= macrocycle [15]aneN_3O_2; Medpt = bis(3-aminopropyl)methylamine; L2 = 1,4,7,10-tetraazabicyclo[5.5.3]pentadecane; TPA = tris(pyridylmethyl)amine; bpy = 2,2′-bipyridine. − [b] Each copper also has a distance of 2.69 Å to another carbonate oxygen. − [c] The magnetic susceptibility was also measured for the isostructural compound $[Cu_3(pip)_3(H_2O)_3(\mu_3\text{-}CO_3)](ClO_4)_4$, and is J = 8.94, zJ' = −0.075 cm^{-1} (ref.[5]). − [d] No intercluster interaction was considered in the fitting procedure. − [e] The magnetic susceptibility was also measured for the related compound $[Cu_3(dpt)_3(\mu_3\text{-}CO_3)](ClO_4)_4$ [dpt = bis(3-aminopropyl)amine] and is J = 15.8, zJ' = −0.015 cm^{-1} (ref.[7]). − [f] Not given.

in a few analogous compounds (see Table 2). In addition, a very weak antiferromagnetic coupling is observed between trinuclear moieties.

As yet only a few compounds of this type have been reported and characterized structurally and magnetically (Table 2). Further research aimed at the synthesis of more examples of this type of compound, using the synthetic methods described in this paper, is currently in progress.

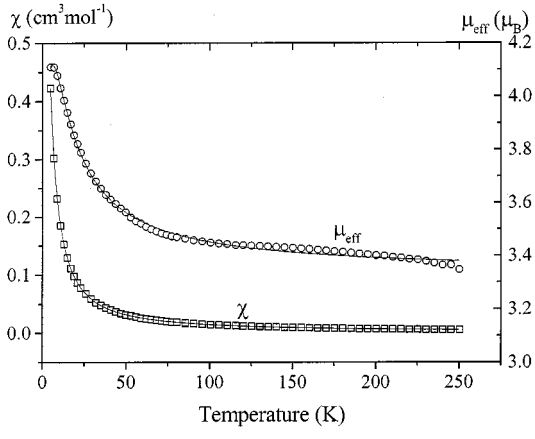

Figure 2. A plot of temperature dependence of χ_m vs. T (□) and μ_{eff} vs. T (○) is shown; the solid line represents the calculated curve for the parameters J = 10.6 cm^{-1}, zj' = −1.2 cm^{-1} and g = 2.22, see text

Experimental Section

General: All chemicals were used as received. The ligand 2,2′-bipyridine was obtained from Acros Organics, Belgium, and used without further purification.

C, H, N, and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland. − Ligand field spectra were obtained on a Perkin−Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. − X-band EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. − FTIR spectra were obtained on a Perkin−Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000−300 cm^{-1}).

Magnetic susceptibility measurements (4−300 K) were carried out using a Quantum Design MPMS-5S SQUID magnetometer (measurements carried out at 1 T). Data were corrected for magnetization of the sample holder, for TIP of copper(II) and for diamagnetic contributions, which were estimated from the Pascal constants.

Synthesis of the Title Compound: 0.3 g (1.3 mmol) of copper(II) tetrafluoroborate and 0.4 g (2.6 mmol) of bpy were each dissolved in 10 mL of ethanol/water (1:1) and the solutions mixed carefully together. A few drops of 2 M sodium hydroxide solution was added in such a way that no precipitation was observed. The mixture was filtered and, after several weeks to a month standing in the open, air blue crystals separated. The crystals were filtered off and washed with ethanol.

When the same procedure was followed in an excicator under a CO_2 atmosphere (dry ice) the crystals were formed within a few days.

Attempts to synthesize the compounds by the addition of sodium or potassium carbonate yielded only the monomeric $Cu(bpy)_2(BF_4)_2$ compound.

Elemental analysis: $C_{63}H_{60}B_4Cu_3F_{16}N_{12}O_7$ (1635.1): calcd. C 46.3, H 3.7, N 10.3, Cu 11.7; found C 46.5, H 3.4, N 10.8, Cu 11.4.

X-ray Data Collection and Structure Determination: A blue prismatic crystal was selected and mounted on a glass fiber using the oil drop method.[24a] Data were collected on a Rigaku AFC-7S diffractometer (graphite-monochromated Mo-$K\alpha$ radiation, ω-2θ scans). The intensity data were corrected for Lorentz and polarization effects, for absorption (psi-scan absorption correction) and extinction. Two tetrafluoroborate groups and an ethanol solvent molecule were disordered. Two positions were assigned to F31, F32, and F33 atoms with a population parameter of 0.5. The other disordered tetrafluoroborate group was refined as two rigid groups with a population parameter of 0.5. The ethanol molecule was refined isotropically. All other non-hydrogen atoms were refined an-

isotropically. H atoms except those belonging to the water molecules were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The structure was solved by direct methods. The programs TEXSAN,[24b] SHELXS-97,[24c] SHELXL-97[24d] were used for data reduction, structure solution, and structure refinement, respectively. Refinement of F^2 was performed against all reflections. The weighted R-factor wR and goodness of fit S are based on F^2, while conventional R-factors are based on F, with F set to zero for negative F^2. Crystal data and numerical details of the structure determination are given in Table 3. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139540. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and details of the structure determination

Crystal data	
Compound	$Cu_3B_4C_{63}F_{16}H_{60}N_{12}O_7$
Mol. wt.	1635
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	13.405(7)
b (Å)	13.691(7)
c (Å)	21.446(8)
α (°)	82.87(4)
β (°)	73.57(4)
γ (°)	64.32(4)
V (Å^3)	3402(3)
Z	2
D_{calc} (g cm^{-3})	1.596
$F(000)$	1658
μ (cm^{-1})	1.035
Crystal size (mm)	0.42 × 0.30 × 0.22
Data collection and refinement	
Radiation	Mo-K_α, 0.71073 Å
Total data coll.	12867
Independent refl. (R_{int})	12383 (0.0221)
Observed refl. [$I > 2\sigma(I)$]	9589
No.of refined params.	979
Final $R1$, $wR2$[a]	0.0677, 0.1836
Min. and max. resd. dens. e·Å^{-3}	1.192, −0.779

[a] Weighting scheme: $w = 1.0/[\sigma^2(F_o^2) + (0.1614 \cdot P)^2 + 16.3151 \cdot P]$.

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