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Synthesis and Crystal Structure of a Compound with Three [2^4.3^1]Adamanzanecopper(II) Species Coordinated to One Carbonate Ion, μ_3-Carbonatotris-{1,4,7,10-tetraazabicyclo[5.5.3]pentadecanecopper(II)} Perchlorate Dihydrate

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The copper(II) complex Cu([2^4.3^1]adz)(H$_2$O)$^{2+}$, where [2^4.3^1]adz is the bicyclic tetramine 1,4,7,10-tetraazabicyclo[5.5.3]pentadecane, reacts with carbonate forming a novel carbonato complex with three copper(II) ions coordinated to one carbonate ion, $[\{Cu([2^4.3^1]adz)\}_3(\mu_3\text{-}CO_3)](ClO_4)_4\cdot 2H_2O$, in a yield of 98%. The structure of $[\{Cu([2^4.3^1]adz)\}_3CO_3](ClO_4)_4\cdot 2H_2O$ has been determined by X-ray diffraction techniques at $T = 120$ K; $M_r = 1321.49$, hexagonal, $P\bar{6}2m$, $a = b = 13.093(3)$, $c = 8.631(2)$ Å, $\gamma = 120°$, $Z = 1$, $D_x = 1.72$ g cm^{-3}, Cu $K\alpha = 1.5418$ Å, $\mu = 41.3$ cm^{-1}, $F(000) = 687$, $R(F4) = 0.0409$ for 862 reflections with $I > 2\sigma(I)$ and $wR(F^2) = 0.0982$ for 903 unique reflections. The geometry around the copper(II) ions is best described as being halfway between trigonal bipyramidal and square pyramidal, the percentage (TBP-SP) being 56.9. Each oxygen atom of the carbonate group is coordinated to a different copper atom, giving a triangular array of copper atoms. The three copper atoms and the carbonate group lie on a crystallographic mirror plane. From the magnetic susceptibility (measured in the temperature range 4–300 K) it is concluded that the copper(II) ions in the trinuclear cation are ferromagnetically coupled with $J = -17.2$ cm^{-1}.

Discrete metal ion carbonate entities, as opposed to infinite networks present in the minerals, are found among the numerous carbonato complexes with transition metal ions. Carbonate may bind to metal ions in different ways. In coordination compounds of transitions metal ions common coordination geometries in mononuclear compounds are monodentate or bidentate carbonates as shown in Figs. 1A and 1B. However, recent studies have shown that carbonate in mono- as well as oligonuclear complexes may exhibit a variety of additional different modes of coordination as summarized by Einstein and Willis.[1]

For a long time the blue mineral azurite,[2,3] $Cu_3(OH)_2(CO_3)_2$, was the only known example where the carbonate ion acts as a tridentate bridge, though in this case also hydroxo bridges connect the copper(II) ions into an infinite network. In 1980 Lippard and co-workers[4] reported a trinuclear copper(II) compound which is the first example of a discrete compound containing a triply coordinated carbonate ions as shown in Fig. 1C for M = Cu(pip)(H$_2$O). For abbreviations of ligands see Experimental section. A similar trinuclear complex with M = Cu(medpt)(ClO$_4$) was recently

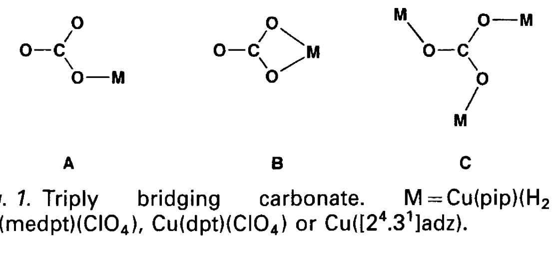

Fig. 1. Triply bridging carbonate. M = Cu(pip)(H$_2$O), Cu(medpt)(ClO$_4$), Cu(dpt)(ClO$_4$) or Cu([2^4.3^1]adz).

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reported by Escuer *et al.*,[5] and is to our knowledge the only other structurally characterized example of this interesting type of coordination. However, a copper(II) complex with dtp reported by Curtis *et al.* probably also has this structure.[6] In this study we present the synthesis and crystal structure of another example of triply bridging carbonate for M = Cu(L), where L is the bowl amine [$2^4.3^1$]adamanzane[7] shown in Fig. 2. The present compound differs from the previous examples in that the copper(II) amine entity is extremely inert (in acid as well as in base) with respect to hydrolysis of the amine, which might simplify studies of its properties in aqueous solutions.

Experimental

Abbreviations. The name [$2^4.3^1$]adamanzane is based upon a simplified nomenclature described recently:[8,9] [$2^4.3^1$]adz = [$2^4.3^1$]adamanzane, 1,4,7,10-tetraazabicyclo-[5.5.3]pentadecane; pip = 2-[2-(pyridyl)ethyliminomethyl]-pyridine; medpt = bis(3-aminopropyl)methylamine; dpt = bis(3-aminopropyl)amine.

Materials and instruments. [Cu([$2^4.3^1$]adz)Br]ClO_4 was synthesized by a previously published method.[9] All other chemicals were of analytical grade and CO_2-free doubly deionized water was used for all measurements. A Cary 3 spectrophotometer was used for spectral measurements, and $\varepsilon/M^{-1}\,cm^{-1}$ values have been calculated using M = mole copper(II) (not mole complex per litre). IR spectra were recorded using a Perkin–Elmer 2000 FT-IR spectrophotometer.

The magnetic susceptibility (cgs units) of a powdered sample was measured with a Faraday balance, described elsewhere,[10] in the temperature range 4–300 K at the field strengths of 1.3 T. The susceptibility data have been corrected for diamagnetism by Pascal's constants.

Analyses. C, H and N analyses were made by the Microanalytical Laboratory at the H. C. Ørsted Institute, Copenhagen, Denmark.

Caution. Mechanical handling or heating of perchlorates represent a potential danger. However, we have never experienced an explosion with the present compound.

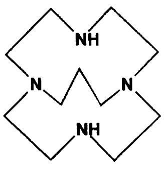

Fig. 2. The bowl amine [$2^4.3^1$]adamanzane.

Syntheses

[{Cu([$2^4.3^1$]adz)}$_3$(μ_3-CO_3)](ClO_4)$_4$·$2H_2O$. μ_3-Carbonato-tris{1,4,7,10-tetraazabicyclo[5.5.3]pentadecanecopper(II)} perchlorate dihydrate. [Cu([$2^4.3^1$]adz)-Br]ClO_4 (456 mg, 1.00 mmol) was dissolved in water (40 ml) at room temperature and added to a solution of Na_2CO_3 (35.0 mg, 0.333 mmol) in water (10 ml). Then 2 M $NaClO_4$ (50 ml) was added and the mixture was stirred for 1 h, during which time a blue precipitate of small crystals was formed. The crystals were separated by filtration, washed once with 50% ethanol (5 ml), twice with 96% ethanol (5 ml) and dried in the air. Yield: 430 mg (98%) of a pure product.

Crystals suitable for X-ray diffraction studies were made in the following way. [Cu([$2^4.3^1$]adz)Br]ClO_4 (456 mg, 1.00 mmol) was dissolved in a mixture of water (50 ml), 1 M NaOH (6 ml) and a saturated solution of sodium perchlorate. The blue solution was left in an open (to allow CO_2 uptake from the air) beaker placed covered with a large beaker (to prevent dust) for one week. During this time dark blue large crystals were formed. The crystals were filtered off, washed with ice-cold water (4 ml), four times with 5-ml portions of 96% ethanol and dried in the air. Yield: 372 mg (84%) of a pure product.

The samples made by the two methods were shown to have identical IR spectra (400–4000 cm^{-1}). Analysis: Calculated for $C_{34}H_{76}N_{12}O_{21}Cl_4Cu_3$: C, 30.90; H, 5.8; N, 12.72. Found: C, 30.84; H, 5.6; N, 12.53.

X-Ray techniques. Crystal and experimental data for the compound are listed in Table 1. Investigation of the Weissenberg films indicated that the Laue class might be $6/mmm$. The crystal was cooled to 120 K using the Cryostream nitrogen gas cooler system.[11] The unit cell was derived from least-squares fit of refined diffractometer setting angles for 25 reflections. Four standards were measured for intensity and orientation control after every 4 h. No fading was observed. The intensities were corrected for Lorentz and polarization effects. Absorption was carried out by an empirical method,[12] in which the crystal shape is approximated by an ellipsoid and the size (in units of μ^{-1}) and orientation are treated as parameters. The refinement of the parameters is based on ψ-scans on three reflections and symmetry equivalents, which amounts to 119 observations. In order not to introduce too high symmetry ($Z = 3$) the structure was solved by direct methods in space group $P3$. The carbon atom in the bridge [C(4)] flips between two equally populated positions, as do the oxygen atoms in the carbonate group. Also the perchlorate ions and water molecules are disordered, the population being 0.5. Even in space group $P1$ the population of the disordered atoms is 0.5. Examination of the atomic coordinates in space group $P3$ showed that the right space group was $P\bar{6}2m$ in agreement with the Weissenberg films. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms could all be located in the difference maps. In

Table 1. Crystal and experimental data.

Formula	$[(C_{11}H_{24}N_4,Cu(II))_3CO_3]^{4+},4ClO_4^- \cdot 2H_2O$
Formula weight	1321.49
Crystal system	Hexagonal
Space group	$P\bar{6}2m$
Unit-cell dimensions:	
a/ Å	13.093(3)
b/ Å	13.093(3)
c/ Å	8.631(2)
γ/°	120.0
Unit-cell volume, V/ Å^3	1281.4(5)
Formula units per unit cell, Z	1
$F(000)$	687
Calculated density, D_x/g cm^{-3}	1.83
Radiation	Cu $K\alpha$
Wavelength, λ/ Å	1.5418
Linear absorption coefficient/cm^{-1}	41.3
Temperature, T/K	120
Crystal description	Blue
Crystal size/mm	0.19 × 0.07 × 0.03
Diffractometer	Enraf-Nonius CAD-4F
Unit-cell determination	
No. of reflections used	25
θ-range/°	10.3–20.9
Intensity data collection	
θ_{max}/°	68
Range of h	−15–15 0–15
Range of k	−15–15+ −15–15
Range of l	−10–0 0–10
Scan mode	ω
Scan range, $\Delta\omega$	$1.10 + 0.35 \tan\theta$
Total number of unique reflections	6909
No. of independent reflections, $[I > 2\sigma(I4)]$	903
Corrections	Lorenz-polarization absorption
Transmission factors	0.4979–0.8728
Structure refinement:	
Minimization of	$\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2$
Anisotropic thermal parameters	All non-hydrogen atoms
Isotropic thermal parameters	Hydrogen atoms
No. of refined parameters	101
Weighting scheme	$[\sigma^2(F^2{}_o) + (0.0360P)^2 + 1.12P]^{-1}$, $P = (F_o{}^2 + 2F_c{}^2)/3$
$R = \Sigma\lvert\,\lvert F_o\rvert - \lvert F_c\rvert\,\rvert/\Sigma\lvert F_o\rvert$	0.0409 (862 reflections)
$wR2 = [\Sigma w\lvert F_o{}^2 - F_c{}^2\rvert^2/\Sigma wF_o{}^4]^{1/2}$	0.0982 (903 reflections)
$S = [\Sigma w(\lvert F_o\rvert^2 - \lvert F_c\rvert^2)^2/(N_{obs} - N_{var})]^{1/2}$	1.20
Final $(\Delta/\sigma)_{max}$	0.07
Final $\Delta\rho_{min}$ and $\Delta\rho_{max}$/e Å^{-3}	−0.67 and 0.25

order to reduce the number of parameters the hydrogen atoms [except those on C(4) and O(water)] were at calculated positions using a riding model with C–H = 0.99 Å and N–H = 0.93 Å and fixed thermal parameters [U(H) = 1.2 times U for attached C or N [U(H[C4]) = 0.03 Å^2 and U(H[water]) = 0.08 Å^3]. The population of the disordered atoms in space group $P\bar{6}2m$ is exactly 0.5, and the structure is refined as a racemic twin. The crystallographic computations were performed with SHELXS86[13] and SHELXL93.[14] The atomic scattering factors were taken from the literature.[15] The PLUTO programme[16] was used for illustration and PLATON[17] for molecular geometry calculations.

The final positional parameters are listed in Table 2. Anisotropic thermal parameters, positional parameters for the hydrogen atoms and lists of observed and calculated structure factors may be obtained from one of the authors (I.S.) on request.

Results and discussion

Crystal structure of $[\{Cu([2^4.3^1]adz)\}_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 2H_2O$. Bond lengths and bond angles of $[\{Cu([2^4.3^1]adz)\}_3(\mu_3\text{-}CO_3)](ClO_4)_4 \cdot 2H_2O$ are listed in Table 3. The labelling of the atoms in the cation is shown in Fig. 3. The compound consists of $[(C_{11}H_{24}N_4Cu)_3CO_3]^{4+}$ cations, ClO_4^- anions and water molecules. The coordination geometry of Cu in $[\{Cu([2^4.3^1]adz)\}_3(\mu_3\text{-}CO_3)]^{4+}$ is best described as being about halfway between the two idealized structures,

Table 2. Fractional atomic coordinates and equivalent isotropic thermal parameters (in Å^2).

Atom	x	y	z	U_{eq}[a]
Cu	0.21132(8)	0.21132(8)	0	0.0208(3)
O(1)[b]	0.1121(7)	0.0353(10)	0	0.034(3)
N(1)	0.2259(4)	0.2259(4)	0.2299(5)	0.0420(18)
N(2)	0.2466(4)	0.3861(6)	0	0.0297(16)
C(1)	0.2218(6)	0.3335(8)	0.2766(6)	0.0571(19)
C(2)	0.1852(4)	0.3826(6)	0.1441(7)	0.0502(18)
C(3)	0.3705(5)	0.4834(7)	0	0.034(2)
C(4)[b]	0.4607(8)	0.4607(8)	0.0745(14)	0.025(3)
C(5)	0	0	0	0.015(3)
Cl(1)	0.43849(15)	0	1/2	0.0306(4)
O(2)[b]	0.5433(6)	0.1029(10)	0.5459(7)	0.058(3)
O(3)[b]	0.4349(7)	0	0.3247(9)	0.046(2)
O(4)[b]	0.3373(6)	0	0.4517(9)	0.034(3)
Cl(2)	0	0	1/2	0.0107(6)
O(5)	0	0	0.3329(14)	0.014(3)
O(6)[b]	0.1027(7)	0	0.4423(8)	0.0267(14)
O(7)[b]	2/3	1/3	0.3167(19)	0.056(4)

[a] $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$. [b] The populations of the atoms are 0.5.

Table 3. Bond lengths (in Å) and bond angles (in °).

Cu–O(1)	2.001(11)	Cu–N(1)	1.993(4)
Cu–N(2)	2.096(7)	O(1)–C(5)	1.300(8)
N(1)–C(1)	1.492(9)	N(2)–C(2)	1.469(6)
N(2)–C(3)	1.480(8)	C(1)–C(2)	1.503(9)
C(3)–C(4)	1.500(11)		
Cl(1)–O(2)	1.416(8)	Cl(1)–O(3)	1.514(8)
Cl(1)–O(4)	1.389(8)	Cl(2)–O(5)	1.442(12)
Cl(2)–O(6)	1.434(8)		
O(1)–Cu-N(1)	94.95(10)	O(1)–Cu-N(2)	156.8(3)
O(1)–Cu-N(2)^{i}	105.2(3)	N(1)–Cu-N(2)	86.4(1)
N(1)–Cu-N(1)^{ii}	169.0(2)	N(2)–Cu-N(2)^{i}	98.0(2)
Cu–O(1)–C(5)	112.2(6)	Cu–N(1)–C(1)	108.2(3)
C(1)-N(1)–C(1)^{i}	116.2(5)	Cu–N(2)–C(2)	98.5(4)
Cu–N(2)–C(3)	119.3(4)	C(2)-N(2)–C(3)	112.0(3)
C(2)-N(2)–C(2)^{ii}	115.7(4)	N(1)–C(1)–C(2)	111.6(5)
N(2)–C(2)–C(1)	111.8(5)	N(2)–C(3)–C(4)	117.6(6)
C(3)–C(4)–C(3)^{i}	117.3(8)		

Symmetry codes: ^{i} y, x, z; ^{ii} $x, y, -z$; The angles in the carbonate ion are all 120.0 due to the special position of the carbon atom [C(5)].

trigonal bipyramidal and square pyramidal, the percentage (TBP-SP) being 56.9. In the trigonal bipyramidal geometry the N(1) and N(1′) atoms occupy the axial positions. The Cu–N(1) bond is somewhat shorter than the Cu–N(2) bond. In the square pyramidal geometry N(2′) occupies the axial position. This is in agreement with the results found in [Cu([2^4.3^1]adz)Br]$^+$.[9]

The conformation of the ligand is the same as found in [Cu([2^4.3^1]adz)Br]$^+$.[9] In the 12-membered ring the 8 carbon atoms are nearly coplanar, with N(1) about 0.7 Å below and N(2) about 0.5 Å above the plane. The ring has *mm* symmetry, N(1) and N(2) being positioned on a crystallographic mirror plane. The N(2)–N(2′) distance between the bridgehead nitrogen atoms is 3.164(10) Å and the N(1)–N(1′) distance is 3.969(6) Å. The two 10-membered rings in the ligand both have *m* symmetry, N(1) and C(4) being positioned on a crystallographic mirror plane. The six-membered ring has an envelope or half boat conformation, and all five-membered rings are in a twist form.

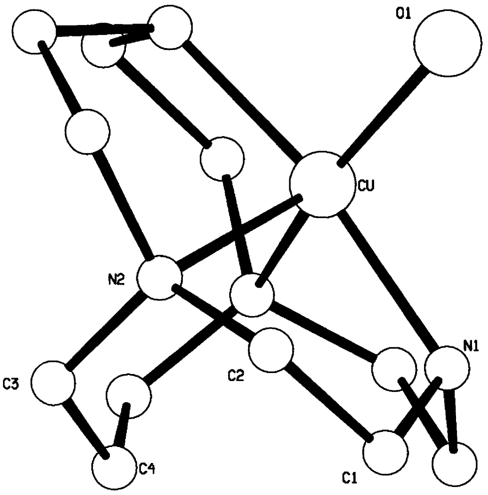

Fig. 3. View of the Cu([2^4.3^1]adz)-O- entity. Only one position for C(4) and O(1) is presented. The carbon atom [C(5)] of the carbonate ion is omitted.

The carbonate group is a triply bridging, tridentate ligand (Fig. 4). This arrangment is also found in the mineral azurite, $Cu_3(OH)_2(CO_3)_2$,[2,3] in [{Cu(pip)(H$_2$O)}$_3$(μ$_3$-CO$_3$)](NO$_3$)$_4$[4] and in [{Cu(medpt)(ClO$_4$)}$_3$(μ$_3$-CO$_3$)]ClO$_4$.[5] The Cu–O bond of 2.001(11) Å is in agreement with those found in azurite and in [{Cu(medpt)(ClO$_4$)}$_3$(μ$_3$-CO$_3$)]ClO$_4$.[5] The unit cell of [{Cu(pip)(H$_2$O)}$_3$(μ$_3$-CO$_3$)](NO$_3$)$_4$ is hexagonal and the space group is $P\bar{6}2c$.[4] The ligand and the nitrate groups are disordered, but not the carbonate group as in the

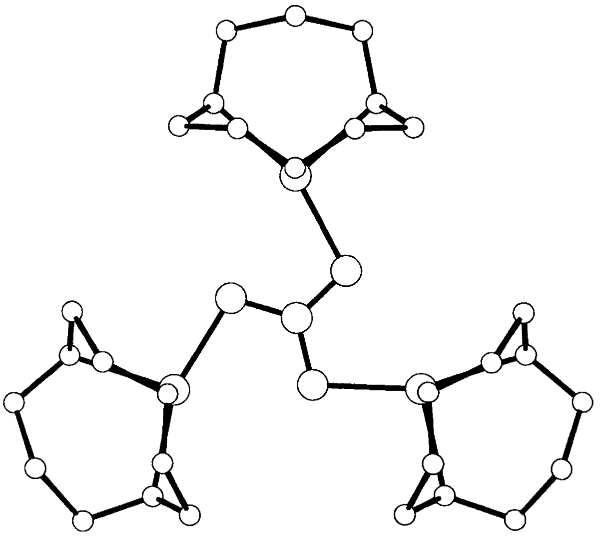

Fig. 4. View of the cation [{Cu([2^4.3^1]adz)}$_3$(μ$_3$−CO$_3$)]$^{4+}$ along the $\bar{6}$-axis. Only one position for O(1) is presented.

present structure. The unit cell of $[\{\mathrm{Cu(medpt)(ClO_4)}\}_3(\mu_3\text{-}\mathrm{CO_3})]\mathrm{ClO_4}$ is reported[5] to be monoclinic, with space group *Cc*. The perchlorate ions are disordered, and the refinement indicates that the crystal is a twin. Our examination of the coordinates in Ref. 5 indicates additional symmetry or pseudosymmetry in the structure. The space group may not be *Cc* but $R\bar{3}$. The only hydrogen bond in the structure is the N(1)–H···O(6) bond of 3.153(10) Å between the ligand and one of the perchlorate ions.

Synthesis and properties. A study of a series of copper(II) coordination compounds with the bowl amine $[2^4.3^1]$adamanzane (Fig. 2) was recently reported.[9] This rigid amine has a time-averaged C_{2v} symmetry, which is maintained in its metal coordination compounds as shown by the crystal structures of the two pentacoordinated compounds $[\mathrm{Cu}([2^4.3^1]\mathrm{adz})\mathrm{Br}]\mathrm{ClO_4}$ and $[\mathrm{Cu}([2^4.3^1]\mathrm{adz})\mathrm{I}]\mathrm{I}$. In aqueous solution these compounds form the aqua complex $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{H_2O})^{2+}$. In connection with a study of the acid–base properties of this ion ($\mathrm{p}K_a = 9.1$) we found that basic solutions when left in the air slowly formed blue crystals. A crystallographic study (see above) of the product established that one carbonate ion had reacted with three copper(II) species as shown in eqn. (1):

$$3\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{H_2O})^{2+} + \mathrm{CO_3}^{2-} \overset{K_f}{\rightleftharpoons} \{\mathrm{Cu}([2^4.3^1]\mathrm{adz})\}_3(\mu_3\text{-}\mathrm{CO_3})^{4+} + 3\mathrm{H_2O} \qquad (1)$$

The trinuclear complex was isolated as the salt $[\{\mathrm{Cu}([2^4.3^1]\mathrm{adz})\}_3(\mu_3\text{-}\mathrm{CO_3})](\mathrm{ClO_4})_4\cdot 2\mathrm{H_2O}$ nearly quantitatively (98%) by mixing the reactants in the ratio 3:1 given by eqn. (1). Preparations using an excess of carbonate afforded lower yields (about 85%).

From spectrophotometric measurements in the visible region it seems clear that the equilibrium above is accompanied by other equilibria, and we have found no conditions for which the triply bridged species is the dominant (>99%) species. Several experiments indicate that the equilibrium constant K_f in eqn. (1) is relatively small.

The visible absorption spectrum of a solution of $[\{\mathrm{Cu}([2^4.3^1]\mathrm{adz})\}_3(\mu_3\text{-}\mathrm{CO_3})](\mathrm{ClO_4})_4\cdot 2\mathrm{H_2O}$ in 1.0 M NaOH is identical to the spectrum of the hydroxo monomer, $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{OH})^+$ (Table 4). The same result was obtained for a 1.96×10^{-3} M solution of the triply bridged copper(II) complex in 0.1 M $\mathrm{Na_2CO_3}$, 0.1 M NaOH, 0.6 M $\mathrm{NaClO_4}$ ($I = 1.0$ M). This shows that the trinuclear complex is completely dissociated into the hydroxo monomer under these conditions, since the perchlorate salt of the trinuclear complex is insoluble in 0.1 M $\mathrm{NaClO_4}$ and it is estimated that it constitutes less than 1% of the total amount of the copper(II) species. Using the known value[9] for $\mathrm{p}K_a$ of $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{H_2O})^{2+}$, it is estimated that $K_f < 1\times10^{15}\ \mathrm{M}^{-2}$ ($I = 1.0$ M, 25 °C).

Table 4. Visible absorption spectra of aqueous solutions[a] of $[\{\mathrm{Cu}([2^4.3^1]\mathrm{adz})\}_3(\mu_3-\mathrm{CO_3})](\mathrm{ClO_4})_4\cdot 2\mathrm{H_2O}$ at 25 °C.

Solvent	$(\varepsilon/\mathrm{M}^{-1}\,\mathrm{cm}^{-1},\ \lambda/\mathrm{nm})_{\mathrm{max}}$[a]
0.10 M $\mathrm{NaHCO_3}$	(141, 622)
0.05 M $\mathrm{NaHCO_3}$, 0.05 M $\mathrm{Na_2CO_3}$	(138, 622)
0.10 M $\mathrm{Na_2CO_3}$	(134, 621)
1 0 M $\mathrm{Na_2CO_3}$	(136, 621)
1.0 M NaOH[b]	(116, 633)
0.1 M $\mathrm{Na_2CO_3}$, 0.1 M NaOH[b,c]	(115, 634)

[a] 1.96×10^{-3} M [molarity with respect to copper(II)]. [b] The spectra of $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{OH})^+$ and $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{OH_2})^{2+}$, respectively, have $(\varepsilon/\mathrm{M}^{-1}\,\mathrm{cm}^{-1},\ \lambda/\mathrm{nm})_{\mathrm{max}} = (118,\ 633)$ and $(\varepsilon/\mathrm{M}^{-1}\,\mathrm{cm}^{-1},\ \lambda/\mathrm{nm})_{\mathrm{max}} = (107,\ 597)$.[9] [c] $I = 1.0$ M, 0.6 M $\mathrm{NaClO_4}$.

The visible absorption spectra of solutions of $[\{\mathrm{Cu}([2^4.3^1]\mathrm{adz})\}_3(\mu_3\text{-}\mathrm{CO_3})](\mathrm{ClO_4})_4\cdot 2\mathrm{H_2O}$ in pure water show a significant dependency on the copper(II) concentration: a 3.6×10^{-3} M solution gave $(\varepsilon/\mathrm{M}^{-1}\,\mathrm{cm}^{-1},\ \lambda/\mathrm{nm}) = (115,\ 608)$, while a 1.12×10^{-4} M solution gave $(\varepsilon/\mathrm{M}^{-1}\,\mathrm{cm}^{-1},\ \lambda/\mathrm{nm}) = (108,\ 604)$. The difference is interpreted as an increasing dissociation of the $\mathrm{Cu_3CO_3}^{4+}$ species at low copper(II) concentration. A complete shift of eqn. (1) to the left should give a mixture of approximately 2/3 of the aqua complex and 1/3 of the hydroxo complex (due to the acid–base reaction between the aqua species and carbonate ions). The spectrum of the 1.12×10^{-4} M solution is similar, but not identical to such a mixture, indicating a (minor) presence of other species, probably carbonato complexes with nuclearities less than three. At very large copper(II) concentration it should in principle be possible to obtain an equilibrium solution in which the triply bridged species is the dominant form. However, in pure water the solubility of the perchlorate salt corresponds to the largest concentration used above, and this concentration is apparently too small to achieve a complete shift to the right in eqn. (1). Measurements of solutions of $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{H_2O})^{2+}$ with a deficiency of carbonate have also been made as an attempt to obtain the spectrum of the trinuclear species. It was anticipated that such solutions would give a mixture of only the mononuclear aqua species and the trinuclear carbonato complex. However, a series of measurements in pure water and in 1 M $\mathrm{NaNO_3}$, respectively, clearly showed that the equilibrium solutions under these conditions are more complicated than anticipated above. At present we therefore do not have an estimate for the spectrum of the triply bridged species.

Addition of an excess of carbonate ions favours the formation of complexes with a $\mathrm{Cu:CO_3}^{2-}$ ratio less than three. The spectra of $[\{\mathrm{Cu}([2^4.3^1]\mathrm{adz})\}_3(\mu_3\text{-}\mathrm{CO_3})](\mathrm{ClO4})_4\cdot 2\mathrm{H_2O}$ in 0.1 M $\mathrm{NaHCO_3}$, 0.05 M $\mathrm{NaHCO_3}$/0.05 M $\mathrm{Na_2CO_3}$, 0.1 M $\mathrm{Na_2CO_3}$ and 1.0 M $\mathrm{Na_2CO_3}$, respectively, are very similar and different from those of the mononuclear species $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{H_2O})^{2+}$ and $\mathrm{Cu}([2^4.3^1]\mathrm{adz})(\mathrm{OH})^+$, as shown in Table 4. It seems unlikely that this is accidental, and we assume that the spectra represent an equilibrium mixture in which one species is dominant. From qualitative solubility experiments we can exclude the possibility that the triply bridged species is present to any significant extent: as mentioned $[\{Cu([2^4.3^1]adz)\}_3(\mu_3\text{-}CO_3)](ClO_4)_4\cdot 2H_2O$ is insoluble in 0.1 M $NaClO_4$, but it dissolves easily in 0.1 M $NaClO_4$, 0.1 M Na_2CO_3 or in 0.1 M $NaClO_4$, 0.1 M $NaHCO_3$. Assuming that copper(II) species with the present amine always have coordination number five,[9] two possible candidates exists: $CuCO_3Cu^{2+}$ and $CuCO_3$ (and its protonated form $CuOCO_2H^+$). On basis of the present data it is not possible to decide which of the two species is the dominant form in the present carbonate/hydrogencarbonate solutions.

Carbonate-related IR-active vibrational frequencies have been assigned[18] as shown in Table 5 and compared with those reported for the structurally characterized (pip)(H_2O) copper(II) complex and the detp(ClO_4) copper(II) complex, which most certainly also has a triply bridged carbonato group.

The magnetic susceptibility of a powdered sample of the perchlorate was measured in the temperature range 4–300 K. The temperature dependence of magnetic susceptibilities $\chi'_{\text{mol.exp}}$ were approximated by eqn. (2).

$$\chi'_{\text{mol,exp}} = \chi'_{\text{mol,calc}} = \frac{-N}{B}\,\frac{\sum_i \frac{\partial E_i}{\partial B}\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} + K \qquad (2)$$

by minimization of eqn. (3):

$$\sum_T \frac{[\chi'_{\text{mol,exp}}(T) - \chi_{\text{mol,calc}}(T)]^2}{\sigma^2(\chi') + \left(\frac{\partial \chi}{\partial T}\right)^2 \sigma^2(T)} \qquad (3)$$

within the framework of nonlinear regression analysis; $\sigma(\chi')$ and $\sigma(T)$ are the estimated standard deviations on the measured magnetic susceptibility and temperature, respectively. K accounts for temperature-independent paramagnetism and minor deviations in the correction for diamagnetism. The energies E_i of the ground-state manifold for the dinuclear complexes were obtained by means of the spin Hamilton operator [eqn. (4)]:

$$\hat{H} = g\mu_B(\hat{S}_a + \hat{S}_b + \hat{S}_c)\cdot \hat{B} + J(\hat{S}_a\cdot\hat{S}_b + \hat{S}_a\cdot\hat{S}_c + \hat{S}_b\cdot\hat{S}_c) \qquad (4)$$

where we have assumed that the g-values for the three copper atoms are identical and isotropic. From the calculations it is concluded that the copper(II) ions in the trinuclear cation are ferromagnetically coupled (Fig. 5). The J-value of $-17.2\ \text{cm}^{-1}$ for the present compound is similar to those reported for other trinuclear copper(II) compounds, as shown in Table 6.

Table 5. Infrared carbonate frequencies for salts of $[Cu(L)]_3(\mu_3-CO_3)^{z+}$ species.

L	Asym. str. μ_3	Out-of-plane μ_2	In-plane def. μ_4
(pip)(H_2O)[a]	1460	840	752
(dtp)(ClO_4)[b]	1475,1425	837	782,672
$[2^4.3^1]$adz[c]	1447	—[d]	735

[a]Ref. 4. [b]Ref 6. [c]This work. [d]Not observed.

Summary

The copper(II) complex with the bowl amine $[2^4.3^1]$adz and water as the fifth donor group reacts with carbonate to form a trinuclear complex $[\{Cu([2^4.3^1]adz)\}_3(\mu_3\text{-}CO_3)]^{4+}$ The thermodynamic stability of the triply bridged complex is relatively small ($K_f < 1\times 10^{15}\ M^{-2}$) and solutions in water give mixtures of its parent mono- and dinuclear carbonato complexes and the mononuclear aqua and hydroxo complexes, whose distribution depends on the copper(II) concentration. The perchlorate salt is scarcely soluble in aqueous solution, compared to the other species present, and can therefore be isolated as a pure salt from solutions in which it is present in even small equilibrium concentrations. In solutions with large $[CO_3{}^{2-}]$ varying from 0.1 to 1.0 M and pH varying from 10 to 12 the dominant species is either $Cu([2^4.3^1]adz)(CO_3)$ or $\{Cu([2^4.3^1]adz)\}_2(\mu_2\text{-}CO_3)^{2+}$. The perchlorate salt of the trinuclear species shows ferromagnetic coupling.

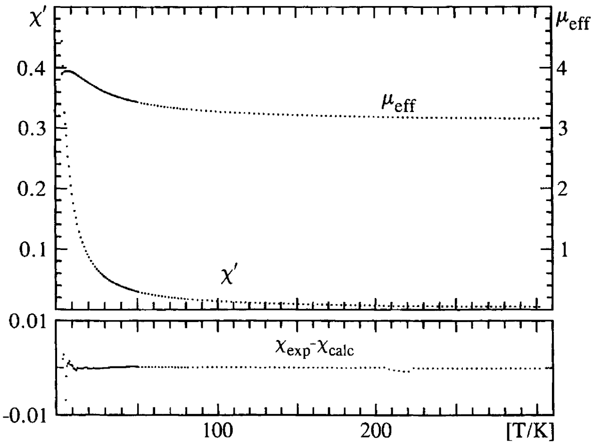

Fig. 5. The magnetic susceptibility (cgs units) and the effective magnetic moment of $[\{Cu([2^4.3^1]adz)\}_3(\mu_3-CO_3)](ClO_4)_4\cdot 2H_2O$. The fitting was accomplished with the operator in eqn. (4) and gave $J = -17.2\ \text{cm}^{-1}$ and $g = 2.061$. The lower graph gives the difference between the measured and calculated susceptibilities.

Table 6. Magnetic data for salts of $[Cu(L)]_3(\mu_3\text{-}CO_3)^{z+}$ species.

L	J^a/cm^{-1}	g	Ref.
$[2^4.3^1]$adz	−17.2	2.061	This work
(medtp)(ClO_4)	−15.8	2.060	5
(pip)(H_2O)[b]	−9.6	2.120	4
(pip)(H_2O)[c]	−8.9	2.139	4

[a]All cited values have been corrected as to correspond to the present definition of the Hamiltonian in eqn. (4) (J and not $-J$ or $-2J$). [b]Nitrate salt. [c]Perchlorate salt.

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