Synthesis and characterization of copper(II) iodo complexes of diethylenetriamine: isolation of an iodo-bridged copper(II) chain

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Abstract

The synthesis and characterization of two complexes of the formulation Cu(dien)I_2, Cu($C_4H_{13}N_3$)I_2, are described. The polymeric complex {[Cu($C_4H_{13}N_3$)I]I}$_n$ crystallizes in the orthorhombic space group *Pnm*2_1 with two molecules in a cell of dimensions $a = 8.873(2)$, $b = 8.890(3)$, $c = 6.658(1)$ Å. The structure has been refined to a final *R* factor of 0.046 based on 596 independent observed intensities. The structure consists of chains of iodide-bridged copper(II) ions along the crystallographic *c* direction. The coordination geometry about copper is tetragonally-elongated (4+2) octahedral, the equatorial plane consisting of three nitrogen atoms from the dien ligand and one iodide while the axial sites are occupied by the other (chain-propagating) iodide ligands. The equatorial Cu–I bond length is 2.585(1) Å while the axial distances are 3.325(1) and 3.371(1) Å. The intrachain Cu–Cu separation is 6.658(1) Å, the *c* axis length, and the bridging Cu–I(2)–Cu angle is 167.7(1)°. The magnetic susceptibility data for the polymeric complex reveal antiferromagnetic coupling. The monomeric complex [Cu(dien)I_2] crystallizes in the monoclinic space group $P2_1/a$ with four molecules in a cell of dimensions $a = 15.140(4)$, $b = 9.690(4)$, $c = 7.526(2)$ Å, $\beta = 105.95(2)$°. The structure has been refined to a final *R* factor of 0.0723 based on 2460 independent observed intensities. The complex is five coordinate, the structure being best described as a distorted trigonal bipyramid in which N(1) and N(3) are axial while N(2), I(1) and I(2) are in the trigonal plane. As is expected for a trigonal bipyramid, copper lies in the trigonal plane. The Cu–I distances are very different, one being 2.619(2) Å while the other is 3.049(2) Å.

Introduction

There are few structurally characterized copper(II) complexes with coordinated iodide, presumably because in the absence of suitable protecting ligands the copper(II) is reduced to copper(I) by iodide ion. There are some well characterized monomeric complexes of this general type [1], but complexes in which two (or more) copper(II) ions are bridged by one or more iodo ligands are very rare. It has been proposed that the copper(II) centers in the complex [Cu_2(cyclops)$_2$I]ClO_4, where cyclops is $C_{11}H_{18}N_4BF_2O_2$, are bridged by a single iodide ion [2], and magnetic studies on this complex reveal antiferromagnetic coupling between the copper centers, but the crystal structure of this complex has not been reported.

During the course of an investigation into the magnetic properties of complexes of copper(II) with diethylenetriamine, we isolated two distinct complexes with the formulation Cu(dien)I_2, or Cu($C_4H_{13}N_3$)I_2. Magnetic studies indicated that one of these complexes exhibits exchange coupling between the copper centers, which suggested the presence of iodo bridges. We here report the synthesis, structural properties and magnetic characterization of these two complexes.

Experimental

Synthesis of the complexes

Polymeric [Cu(dien)I_2]$_n$

A solution of 1.1 ml (10 mmol) of the ligand in 10 ml H_2O was added to a solution of 2.54 g (10 mmol) $CuSO_4 \cdot 5H_2O$ in 10 ml water. The solution

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turned deep blue, characteristic of complexed copper(II) ions. After 10 min of continuous stirring, 3.9 g (23.5 mmol) KI in 25 ml water was added. The deep blue color of the solution intensified, and a small quantity of gray–brown precipitate formed. The solution was stirred vigorously for a further 1.5 h and then filtered to remove the gray–brown solid. Approximately 30 ml ethanol (96%) were added to the filtrate. After two days at room temperature, very large dark green diamond shaped crystals were obtained. The crystals were separated, washed with ethanol (99%), and air dried. *Anal.* Calc. for $CuC_4H_{13}N_3I_2$: C, 11.43; H, 3.12; N, 9.99; I, 60.36. Found: C, 11.61; H, 3.06; N, 9.97; I, 61.39%.

Monomeric [Cu(dien)I$_2$]

The monomeric complex was obtained in an entirely analogous fashion as above but with the use of a 10% excess of the ligand. The crystals are green prisms, paler in color than those of the polymer. *Anal.* Calc. for $CuC_4H_{13}N_3I_2$: C, 11.43; H, 3.12; N, 9.99; I, 60.36. Found: C, 11.29; H, 3.36; N, 10.09; I, 61.26%.

Magnetic measurements

Static magnetization data were collected on a powdered sample of the polymeric species using a Princeton Applied Research Model 155 vibrating sample magnetometer (VSM) equipped with a Janis Research Co. liquid helium dewar. The magnetometer was calibrated with $HgCo(NCS)_4$ [3]. The VSM magnet (Magnion H-96), power supply (Magnion HSR-1365), and associated field control unit (Magnion FFC-4 with a Rawson-Lush Model 920 MCM rotating coil gaussmeter) were calibrated against NMR resonances (^1H and ^3Li). A calibrated GaAs diode was used to monitor the sample temperature.

Magnetic susceptibility data were collected in the temperature range 1.8–70 K with a magnetic field of 10 kOe. The data were corrected to compensate for the diamagnetism of the constituent atoms and for the temperature independent paramagnetism of the copper(II) ions [4].

EPR spectra

EPR spectra were recorded at X-band on a Varian E-109 spectrometer with a rectangular TE_{102} cavity. The magnetic field was calibrated with a DPPH marker, and the frequency was monitored with a Hewlett-Packard 5245L frequency counter. The spectra of a powdered sample of the polymer sealed in a quartz tube were collected at room and liquid nitrogen temperatures.

X-ray structure determinations

Polymeric [Cu(dien)I$_2$]$_n$

The data were collected and reduced in the manner described by Graves and Hodgson [5] on an Enraf-Nonius CAD-4 diffractometer. The cell constants were determined by a least-squares fit to the angular settings of 25 intense data. The near equality of the *a* and *b* axial lengths suggested a tetragonal cell, but an analysis of the intensities of reflections of the types (hkl), (khl) and ($k\bar{h}l$) failed to reveal four-fold symmetry. Hence, the system was demonstrated to be orthorhombic.

Diffraction data were collected on the CAD-4 diffractometer equipped with a molybdenum tube ($\lambda K\alpha_1 = 0.70926$ Å; $\lambda K\alpha_2 = 0.71354$ Å) and a graphite monochromator. Crystal data and experimental parameters are tabulated in Table 1. The data were corrected for Lorentz–polarization effects and for absorption using an empirical absorption correction. A total of 931 independent data was collected, of which 596 had $I \geqslant 3\sigma(I)$.

The structure was solved by the Patterson method. Definitive systematic absences are $k+l=2n+1$ for $0kl$. These are consistent with the space groups $Pnmm$, $Pn2_1m$ and $Pnm2_1$, which are alternate settings of $Pmmn$ [No. 59] and $Pmn2_1$ [No. 31]. The positions of the iodine and copper atoms were deduced from a Patterson function and the remaining non-hydrogen atoms were located in a difference Fourier summation calculated in the centrosymmetric space group. Least-squares refinement gave values of 0.145 and 0.153

TABLE 1. Crystallographic and data collection parameters

Complex	polymer	monomer
Formula	$CuC_4H_{13}N_3I_2$	$CuC_4H_{13}N_3I_2$
Color	dark green	green
System	orthorhombic	monoclinic
Space group	$Pnm2_1$	$P2_1/a$
Cell dimensions		
a (Å)	8.873(2)	15.140(4)
b (Å)	8.890(3)	9.690(4)
c (Å)	6.658(1)	7.526(2)
β (°)		105.95(1)
Volume (Å^3)	525.1(4)	1061.6(5)
Z	2	4
Absorption coefficient (mm^{-1})	8.04	7.77
Index ranges	$0 \leqslant h \leqslant 12$	$0 \leqslant h \leqslant 22$
	$0 \leqslant k \leqslant 12$	$0 \leqslant k \leqslant 14$
	$0 \leqslant l \leqslant 9$	$-11 \leqslant l \leqslant 11$
No. reflections	931	3114
Observed reflections ($I > 3\sigma(I)$)	596	2460
R	0.046	0.0723
R_w	0.051	0.0845

for R and R_w, respectively. Removal of one mirror plane, thereby changing the space group to $Pnm2_1$, reduced these values to 0.129 and 0.144, and application of the absorption correction yielded values of 0.060 and 0.067, respectively. The z coordinates of the C and N atoms showed a tendency to oscillate about the pseudo-mirror plane at $z = 1/4$, which slowed refinement of the structure, and the z coordinate of atom C(1) was eventually fixed in order to overcome this problem. A difference Fourier map revealed the positions of the seven independent hydrogen atoms. No attempt was made to vary the hydrogen atom parameters in the least-squares process, but other atoms were refined anisotropically. The final values of the agreement factors were $R = 0.046$, $R_w = 0.051$. A listing of atomic positional parameters is given in Table 2.

It was apparent to us at an early stage of the refinement that the present cell was very similar to that of a related complex, dibromo[*N*-(2-hydroxyethyl)ethylenediamine]copper(II), whose structure has been reported by Pajunen and coworkers [6]. The cell determined by Pajunen has an *a* axis length roughly double that of ours, and the resultant space group is $Pna2_1$. We attempted, therefore, to look for data with half-integer *h* values (in our cell), which would indicate that the *a* axis was indeed double that which we had assumed, but failed to find any. We then attempted to fit our structure into the cell of Pajunen and coworkers by converting our Cu and I coordinates to those appropriate for their cell and appropriately reindexing our data, but refinement was entirely unsuccessful. Finally, we attempted simply to assign to our Cu and I atoms the coordinates Pajunen *et al.* found for their Cu and Br atoms, again without success. Consequently, we are satisfied that the similarity between our cell and that of these other workers is coincidental.

Monomeric [Cu(dien)I₂]

The structure was determined on a Nicolet R3m/V diffractometer equipped with a molybdenum tube ($\lambda K\alpha_1 = 0.70926$ Å; $\lambda K\alpha_2 = 0.71354$ Å) and a graphite monochromator. Crystal data and experimental parameters are tabulated in Table 1. The data were corrected for Lorentz–polarization effects and for absorption. A total of 3114 unique reflections was collected, of which 2460 had $I \geqslant 3\sigma(I)$.

The structure was solved by direct methods and difference Fourier methods and refined by least-squares techniques; the programs used were from the SHELXTL system. Hydrogen atoms were assigned fixed positions while other atoms were refined anisotropically. The final values of the conventional R factors were $R = 0.0723$, $R_w = 0.0845$, based on 2460 independent data with $I > 3\sigma(I)$. The final values of the atomic positional parameters, along with their estimated standard deviations, are presented in Table 3. See also 'Supplementary material'.

TABLE 2. Atomic positional parameters for polymeric [Cu(dien)I$_2$]

Atom	x	y	z
I(1)	0.1568(1)	0.0000	0.250
I(2)	−0.1751(2)	0.0000	0.748(1)
Cu	−0.1346(2)	0.0000	0.251(2)
N(1)	−0.158(1)	0.223(1)	0.247(8)
N(2)	−0.362(1)	0.000	0.221(2)
C(1)	−0.314(1)	0.264(1)	0.250
C(2)	−0.421(1)	0.141(2)	0.197(2)

Results and discussion

The synthesis of a complex formulated as Cu(dien)I$_2$ was first reported by Mann in 1934 [7]. The present syntheses differ from that reported by Mann, in that he noted that he was able to obtain the product only after removing a product he formulated as [Cu$_2$(dien)$_3$I$_4$] from a basic aqueous solution of dien, KI, and hydrated CuSO$_4$ and then bubbling CO$_2$ through the filtrate to slightly acidify it. The complex [Cu$_2$(dien)$_3$I$_4$] was not identified in the present work.

Description of the structures

Polymeric [Cu(dien)I₂]ₙ

The structure consists of polymeric chains of copper(II) ions bridged by single iodide ions along the crystallographic *c* axis. Each unit in the chain is related to the next by a 2_1 symmetry operation. A view of a Cu–I(2)–Cu–I(2)–Cu segment of the chain is given in Fig. 1. Principal distances and angles in the cation are listed in Tables 4 and 5, respectively.

TABLE 3. Atomic positional parameters ($\times 10^4$) for monomeric [Cu(dien)I$_2$]

Atom	x	y	z
I(1)	9055(1)	352(1)	6854(1)
I(2)	8765(1)	5064(1)	7499(1)
Cu	8267(1)	2171(2)	8493(2)
N(1)	7113(6)	2344(10)	6467(11)
N(2)	7444(5)	2567(9)	10162(10)
N(3)	9297(6)	2373(9)	10800(11)
C(1)	6324(7)	2465(13)	7266(15)
C(2)	6613(7)	3229(14)	9031(16)
C(3)	8024(8)	3331(14)	11769(15)
C(4)	8913(8)	2586(13)	12395(12)

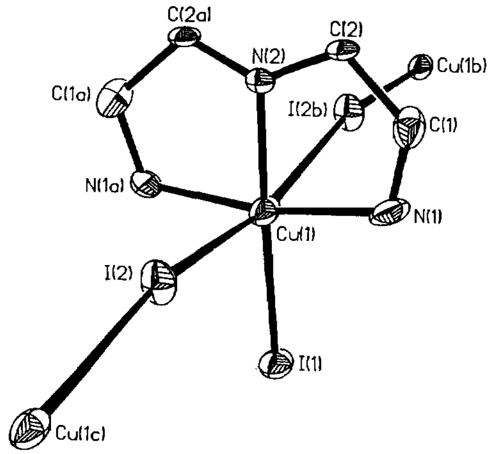

Fig. 1. View of the geometry around the copper(II) center in polymeric [Cu(dien)I_2]. Atoms labelled 'a' are related to the parent atoms by reflection across the plane through Cu, I(1), I(2) and N(2); atoms labelled 'b' and 'c' are related to the parent atoms by translation along the *c* direction. Hydrogen atoms are omitted for clarity.

TABLE 4. Bond lengths (Å) in polymeric [Cu(dien)I_2]

Atoms	Distance
Cu-I(1)	2.585(1)
Cu-I(2b)[a]	3.371(1)
Cu-N(2)	2.030(7)
C(1)-C(2)	1.491(9)
Cu-I(2)	3.325(1)
Cu-N(1)	1.998(5)
N(1)-C(1)	1.429(8)
C(2)-N(2)	1.366(8)

[a] Related to I(2) by translation along *c*.

TABLE 5. Bond angles (°) in polymeric [Cu(dien)I_2]

Atoms	Angle
I(1)-Cu-I(2)	96.4(3)
I(1)-Cu-I(2b)	95.9(3)
I(1)-Cu-N(1)	96.1(2)
I(1)-Cu-N(2)	174.0(7)
I(2)-Cu-I(2b)	167.7(1)
I(2)-Cu-N(1)	90.2(13)
I(2)-Cu-N(2)	89.6(6)
I(2b)-Cu-N(1)	88.5(13)
I(2b)-Cu-N(2)	78.2(6)
N(1)-Cu-N(1a)	167.8(5)
N(1)-Cu-N(2)	83.9(2)
Cu-N(1)-C(1)	110.8(4)
Cu-N(2)-C(2)	113.0(4)
C(2)-N(2)-C(2a)	133.1(9)
N(1)-C(1)-C(2)	115.1(7)
N(2)-C(2)-C(1)	114.0(7)
Cu-I(2)-Cu(c)	167.7(1)

The intrachain Cu–Cu separation is 6.658(1) Å, the *c* axis length. The chain-propagating Cu–I(2) bonds are slightly asymmetric, with lengths of 3.325(1) and 3.371(1) Å. The terminal Cu–I(1) bond length is 2.585(1) Å.

The geometry about each copper(II) center is axially elongated (4 + 2) octahedral, the equatorial ligating atoms being three nitrogen atoms from the dien ligand and one iodide ion (I(1)), while the axial sites are occupied by the chain-propagating I(2) ions. The copper center lies on a mirror plane which bisects the dien ligand, passing through N(2), and also contains atoms I(1) and I(2).

There are no other published reports of crystallographically characterized iodo-bridged copper(II) complexes, and few other suggestions of such complexes. As was noted above, however, the structure of the closely related complex dibromo[*N*-(2-hydroxyethyl)ethylenediamine]copper(II) is known [6]. In this bromo-bridged complex the equatorial Cu–Br(1) bond length is 2.362(3) Å and the bridging Cu–Br(2) distances are 3.094(8) and 3.325(8) Å. Hence, in both the bromo-bridged structure and in the present structure the equatorial, terminal Cu–X distance is approximately 0.8 Å shorter than the average of the axial, chain-propagating Cu–X bond lengths. In both of these complexes, the intrachain Cu–X distances are only approximately 0.2 Å less than the sum of the van der Waals radii of the atoms involved. Hence, in principle, both could be viewed as isolated monomers rather than polymers. Our description of the iodo complex (and, by inference, the bromo complex) as a chain polymer, however, is strongly supported both by the magnetic properties of the complex and by the existence of an entirely different monomeric isomer with far longer non-bonded Cu···I separations (*vide infra*).

Additional support for this polymeric view comes from Tebbe's study of copper(II) complexes of polyiodide ions [8]. In the structure of [Cu(NH_3)$_4$(I_4)], the I_4^{2-} ions link the Cu(II) centers in polymeric zigzag chains with Cu–I separations of 3.226(2) Å. Similarly, the structure of [Cu(NH_3)$_4$(I_3)]I_3 [8] is polymeric with Cu(II)–I distances of 3.294(2) Å. Both of these values are comparable with the present values of 3.325(1) and 3.371(1) Å. It should be noted, however, that in anhydrous copper(I) iodide, the average Cu(I)–I distance is only 2.616(5) Å [9], comparable with the terminal Cu(II)–I distances found here.

Monomeric [Cu(dien)I_2]

The structure consists of monomeric [Cu(dien)I_2] units which are well separated from each other. A view of the complex is given in Fig. 2, and important

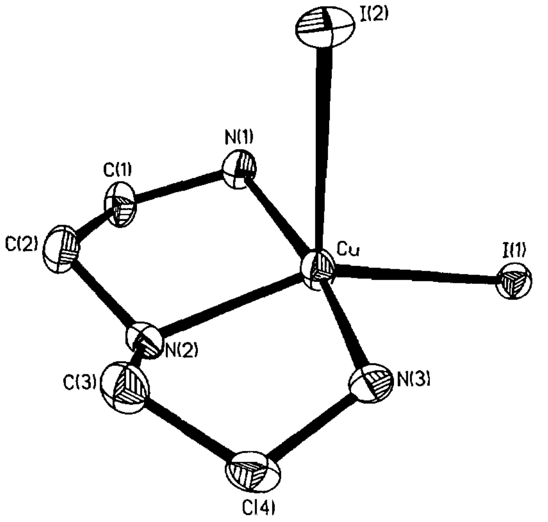

Fig. 2. View of the geometry around the copper(II) center in monomeric [Cu(dien)I_2]. Hydrogen atoms are omitted for clarity.

TABLE 6. Bond lengths (Å) in monomeric [Cu(dien)I_2]

Atoms	Distance
I(1)–Cu	2.619(2)
Cu–N(1)	1.986(7)
Cu–N(3)	1.999(7)
N(2)–C(2)	1.460(13)
N(3)–C(4)	1.485(15)
C(3)–C(4)	1.485(17)
I(2)–Cu	3.049(2)
Cu–N(2)	2.034(9)
N(1)–C(1)	1.482(15)
N(2)–C(3)	1.483(13)
C(1)–C(2)	1.478(16)

bond lengths and angles are listed in Tables 6 and 7, respectively.

The geometry at the copper(II) center is five coordinate, the structure being best described as a distorted trigonal bipyramid in which N(1) and N(3) are axial while N(2), I(1) and I(2) are in the trigonal plane. As is expected for a trigonal bipyramid, copper lies in the trigonal plane (average deviation from the four-atom plane, 0.002 Å). The principal distortion from trigonal pyramidal geometry is in the angles in the 'trigonal' plane; in the idealized case these should all be 120°, but in the present structure they range from 102.3(2)–148.6(2)°. Obviously, there is an alternate description of the complex as a distorted tetragonal pyramid, where one iodine atom (I(2)) is axial while the three ligand nitrogen atoms and the other iodine atom are equatorial. The distortions from idealized tetragonal pyramidal geometry are severe, however, the *trans* angles N(1)–Cu–N(3) and N(2)–Cu–I(1) being 166.0(4) and 148.6(2)°, respectively. More importantly, the equatorial 'plane' is severely distorted from planarity, and the copper atom lies in this least-squares plane; in a tetragonal pyramid, the copper atom would be expected to sit above the plane, on the same side as I(2).

TABLE 7. Bond angles (°) in monomeric [Cu(dien)I_2]

Atoms	Angle
I(1)–Cu–I(2)	109.2(1)
I(2)–Cu–N(1)	87.6(3)
I(2)–Cu–N(2)	102.3(2)
I(1)–Cu–N(3)	97.3(3)
N(1)–Cu–N(3)	166.0(4)
Cu–N(1)–C(1)	109.4(6)
Cu–N(2)–C(3)	105.8(7)
Cu–N(3)–C(4)	109.3(6)
N(2)–C(2)–C(1)	107.4(10)
N(3)–C(4)–C(3)	109.5(8)
I(1)–Cu–N(1)	96.5(3)
I(1)–Cu–N(2)	148.6(2)
N(1)–Cu–N(2)	84.2(3)
I(2)–Cu–N(3)	86.4(3)
N(2)–Cu–N(3)	84.8(3)
Cu–N(2)–C(2)	107.4(7)
C(2)–N(2)–C(3)	118.6(9)
N(1)–C(1)–C(2)	109.4(8)
N(2)–C(3)–C(4)	107.3(10)

The Cu–I bond lengths in the complex are very different from each other. The Cu–I(1) bond length of 2.619(2) Å is comparable to the terminal Cu–I(1) distance of 2.585(1) Å found in the polymeric analogue, but the Cu–I(2) distance of 3.049(1) is much longer than these values. While there are few Cu–I distances with which to compare the present results, a bond length of 2.70 Å was reported for [Cu(bpy)$_2$I]$^+$ [1]. While Barclay *et al.* [1] regarded this distance as 'normal' since they report the sum of the covalent radii of Cu and I as approximately 2.68 Å, Zhdanov [10] gives a smaller value of 2.61 Å. Hence, the present Cu–I(2) distance is abnormally long, while the Cu–I(1) separations in both species are similar to that predicted on the basis of Zhdanov's compilation. The Cu–N(1) and Cu–N(3) distances of 1.986(7) and 1.999(7) are not significantly different, but are slightly shorter than the Cu–N(2) distance of 2.034(9) Å involving the secondary amine nitrogen atom. The metrical parameters in the polymeric complex are entirely in accord with this result, the analogous distances being 1.998(5) and 2.030(7) Å to the primary and secondary amine nitrogen atoms, respectively.

Electron paramagnetic resonance spectroscopy

The EPR spectrum of a powdered sample of the polymeric complex was obtained at 295 and 77 K. Each spectrum consists of a single symmetrical resonance which reveals low g factor anisotropy ($g_{\parallel} \sim g_{\perp}$) and an average g factor of 2.073. No increase in resolution of hyperfine structure was found in the spectrum at 77 K.

Magnetic properties

The temperature dependence of the magnetic susceptibility of the polymer complex was measured in the range 1.8–70 K. A linear least-squares fit of the inverse susceptibility data to the Curie–Weiss equation

$$\chi = \frac{C}{T-\theta}, \qquad C = \frac{Ng^2\mu_B^2}{3k} S(S+1)$$

gave values of $C = 0.402$ and $\theta = -1.1$. For $S = 1/2$, this value of C corresponds to a g of 2.071, in good agreement with the value of 2.073 determined from the EPR spectra. The negative value of θ indicates antiferromagnetic exchange coupling with a small (negative) value of the coupling parameter J. The susceptibility data can be fitted to the one-dimensional isotropic Heisenberg chain model [11], yielding a value of $J = -1.5$ cm^{-1} with g fixed at 2.073. It would, of course, be of value to compare this result with magnetic parameters for the related bromo-bridged species discussed above [6], but magnetic data for that complex have not been reported.

Supplementary material

Tables S1 and S2 (hydrogen atom positional parameters), Tables S3 and S4 (anisotropic thermal parameters), Tables S5 and S6 (observed and calculated structure amplitudes); are available from author D.J.H. on request.

Acknowledgements

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