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CRYSTAL STRUCTURE AND MAGNETISM OF 4,4'-BIPYRIDYLIUM DI- μ -BROMOTETRABROMODICUPRATE(II)

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A new bromocuprate complex of formula $C_{10}H_{10}N_2Cu_2Br_6$ has been synthesized and its crystal structure investigated by single-crystal X-ray methods. Stable, black, needle-like crystals are isostructural with the analogous chloride compound.¹ The crystals are triclinic, $a = 4.1018(5)$, $b = 10.2755(10)$, $c = 11.0355(9)$ Å, $\alpha = 113.894(7)$, $\beta = 94.975(8)$, $\gamma = 95.935(9)^\circ$. The structure was refined by least-squares methods to $R = 0.031$ and $R_w = 0.038$ for 1930 reflections. It consists of cationic columns formed by stacking of planar $(4,4'\text{-bipy } H_2)^{2+}$ cations and anionic columns formed by stacking of nearly planar $Cu_2Br_6^{2-}$ anions. Cationic and anionic columns are parallel to the needle axis. The geometry and interionic interactions for the chloride and bromide crystals were compared. The EPR spectrum of a polycrystalline sample of the complex displayed only one broad line centred at 2.08 (T = 293 K). Variable temperature (ca 4.2–290 K) magnetic susceptibility data indicated an antiferromagnetic superexchange interaction between copper(II) centres much stronger than observed for the chloride analogue.

Keywords: di- μ -Bromotetrabromocuprate(II) 4,4'-bipyridylum, X-ray structure, magnetics

INTRODUCTION

The structure of copper(II) halide salts have been of particular interest as regards attempts of an understanding of the correlations between structural parameters and magnetic properties in inorganic systems. Structurally, the coordination geometry of the copper(II) ion is very differentiated.² Coordination numbers range from 4 to 6 but coordination geometries are rarely regular.^{3,4} They include geometries that are four-coordinate, ranging from square-planar to distorted tetrahedral, five coordinate, with variation among square-pyramidal, trigonal-bipyramidal, and other 4 + 1 geometries, and six-coordinate with a 4 + 2 geometry. The differences among coordination geometry are particularly evident in copper(II) halide salts, since the halide ions impose little stereochemical restriction. Additionally, the halide ion is an effective bridging ligand, but this too imposes few steric hindrances upon coordination geometry. These factors provide a mechanism whereby magnetic superexchange pathways may be systematically varied. Magnetostructural correlations for these salts are of interest due to effects of bridging Cu-X-Cu bond angles and coordination geometries on the values of the magnetic coupling constants.

In this paper we report the synthesis, X-ray structure determination and magnetic

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properties of 4,4'-bipyridylum di- μ -bromotetrachlorodicuprate in order to compare structure and properties with those of 4,4'-bipyridylum di- μ -bromotetrachlorodicuprate.¹⁻⁵

EXPERIMENTAL

Preparation

0.60 g (0.0025 mol) of $\text{CuBr}_2 \cdot \text{H}_2\text{O}$ was dissolved in 40 cm³ of water; 0.39 g (0.0025 mol) of 4,4'-bipy was dissolved in 50 cm³ of water and 10 cm³ of 40% HBr was added. The hot solutions were added together and the green mixture was heated for 10 minutes. Slow cooling with simultaneous slow evaporation deposited needle-like black crystals of $\text{C}_{10}\text{H}_{10}\text{N}_2\text{Cu}_2\text{Br}_6$. Found: C, 15.74; H, less than 1; N, 3.65; Br, 59.5%. Calculated: C, 15.71; H, 0.13; N, 3.66; Br, 62.8%.

Crystal data

$\text{C}_{10}\text{H}_{10}\text{N}_2\text{Br}_6\text{Cu}_2$, $M = 382.4$, triclinic, $a = 4.1018(5)$, $b = 10.2755(10)$, $c = 11.0355(9)$ Å, $\alpha = 113.89(7)$, $\beta = 94.975(8)$, $\gamma = 95.935(9)^\circ$; $V = 418.75$ Å³, $F(000) = 348$, $Z = 1$, $D_c = 3.032$ g cm⁻³, $\lambda(\text{MoK}\alpha) = 0.71069$ Å, $\mu(\text{MoK}\alpha) = 167.2$ cm⁻¹; space group $P1$ (from structure determination).

Diffraction data collection

Diffraction data were collected at 293 K from a well-formed single crystal of size 0.5 × 0.3 × 0.2 mm on a NONIUS CAD 4 diffractometer with a graphite monochromator. X-ray intensity data for 2892 unique reflections were measured in the $\lambda/2\theta$ scan mode, up to $\sin \theta/\lambda = 0.64$ Å⁻¹, 1930 of which with $I > 36$ (I) were used for the structure determination. Accurate cell parameters and the orientation matrix were determined from a least-squares treatment of the angular settings of 25 high-order reflections. The scan speed depended upon the intensity (from 1 to 6° min⁻¹). After every 75 reflections three standard reflections were measured to check for reorientation and radiation damage. The intensity data were empirically corrected for absorption, using 4 scans around the diffraction vectors of 7 selected reflections. The observed transmission was from 0.48 to 0.90.

Structure solution

The structure was solved by direct and Fourier methods. Positional and anisotropic thermal parameters for all non-hydrogen atoms were refined by a full-matrix least-squares technique. Hydrogen atoms were included in the structure factors from calculated positions (assuming 1.08 Å C-H and N-H distances, and U_H values of 0.04 Å²), but were not refined. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = [(F_o)]^2 + 0.003 F_o^2$. Refinement was terminated when the maximum shift in any parameter was < 0.1. The final R was 0.0308 and $R_w = 0.0385$. The final difference Fourier map showed a maximum density of 0.7 eÅ⁻³ located near the Cu atom. The final atomic parameters are given in Table I*. Most of the computations were performed with the SHELX-76 crystal structure determination program⁶ on an AMSTRAD 1512 minicomputer.

* A list of observed and calculated structure factors and anisotropic thermal parameters is available from the Editor.

TABLE I
Final atomic coordinates $\times 10^5$ for Cu and Br, $\times 10^4$ for C and N, and $\times 10^3$ for H atoms.

	<i>x/a</i>	<i>x/b</i>	<i>z/c</i>
Cu	67037(12)	9995(5)	-9026(4)
Br(1)	110244(12)	29961(5)	-26931(5)
Br(2)	59886(11)	5551(4)	-32018(4)
Br(3)	26134(10)	-11241(4)	-13724(4)
C(1)	6783(13)	5520(5)	2560(4)
C(2)	5378(13)	4778(4)	3238(4)
C(3)	5742(9)	5398(4)	4619(4)
C(4)	7522(12)	6783(4)	5299(4)
C(5)	8994(11)	7473(4)	4601(5)
N	8535(9)	6839(4)	3264(4)
H(1)	646	505	147
H(2)	403	370	267
H(4)	785	731	638
H(5)	1031	854	512
H(N)	964	742	274

Magnetic measurements

Magnetic susceptibilities of a polycrystalline sample of $(4,4'\text{-bipyH}_2)\text{Cu}_2\text{Br}_6$ were measured by the Faraday method over the temperature range 4.2–290 K, using a Cahn RG-HV electrobalance. The applied magnetic field was 6.25 KOe. The calibrant employed was $\text{HgCo}(\text{NCS})_4$, for which the magnetic susceptibility was taken as $16.44 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$.⁷

The correction for diamagnetism of the constituent atoms was calculated by use of Pascal's constants⁸ and found to be $-330 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The value $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ was used for the temperature-independent paramagnetism of the copper(II) ion. Magnetism of a sample was found to be field independent. The effective magnetic moment was calculated from the usual equation.

EPR measurements

The EPR spectra at room temperature and 77 K were recorded on a JEOL-ME X-band spectrometer using a nuclear magnetometer (MJ 110R) and microwave frequency meter (JES-SH-30X) and usual EPR standards.

Electronic spectra

Reflectance spectra for the diluted compound in Li_2CO_3 were measured in the range 200–700 nm on a Hitachi spectrophotometer (Model 356) and that of an undiluted sample on a Beckman UV 5240 spectrophotometer (400–1000 nm).

RESULTS AND DISCUSSION

The compound consists of discrete $\text{Cu}_2\text{Br}_6^{2-}$ and $(4,4'\text{-bipyH}_2)^{2+}$ ions and is isostructural with the chloride salt $(4,4'\text{-bipyH}_2)\text{Cu}_2\text{Cl}_6$.¹ Figure 1 shows the label-

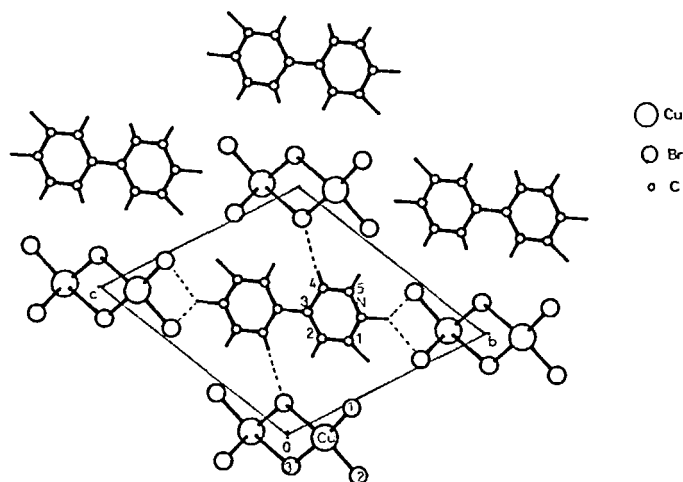


FIGURE 1 Packing of the ions in the unit cell.

TABLE II
Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses.*

a. Lengths

Cu-Br(1)	2.3895(7)	Br(1)-Cu-Br(2)	94.44(3)
Cu-Br(2)	2.3744(6)	Br(2)-Cu-Br(3)	90.61(2)
Cu-Br(3)	2.4536(6)	Br(3)-Cu-Br(3')	83.72(2)
Cu-Br(3')	2.4513(6)	Br(1)-Cu-Br(3')	90.92(2)
Cu-Br(1'')	3.1991(7)	Br(1)-Cu-Br(3)	173.60(3)
Cu-Br(3''')	3.3620(7)	Br(2)-Cu-Br(3')	172.68(3)
Cu-Cu	3.6529(7)	Br(1'')-Cu-Br(3''')	176.07(4)
		Cu-Br(3)-Cu	96.28(2)

b. Angles

C(1)-C(2)	1.386(8)	C(1)-C(2)-C(3)	120.2(4)
C(2)-C(3)	1.380(6)	C(2)-C(3)-C(4)	118.2(4)
C(3)-C(4)	1.395(5)	C(3)-C(4)-C(5)	120.1(4)
C(4)-C(5)	1.368(8)	C(4)-C(5)-N	120.0(4)
C(5)-N	1.336(6)	C(2)-C(1)-N	119.1(4)
C(1)-N	1.344(5)	C(1)-N-C(5)	122.3(4)
C(3)-C(3')	1.513(7)		

c. Proposed donor-acceptor hydrogen bond distances and angles.

N-H... Br(1)	2.57	N-H... Br(1)	132.9
N-H... Br(2)	2.45	N-H... Br(2)	138.5

d. Intermolecular distances <math>< 3.5 \text{ \AA}</math>

H(4)... Br(3')	2.80
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* Atoms marked with one prime are related to those at x, y, z by the centre of symmetry at $0, 0, 0$, or $0.5, 0.5, 0.5$, with two primes by a negative translation along the x axis, and with three primes by a positive translation along the x axis.

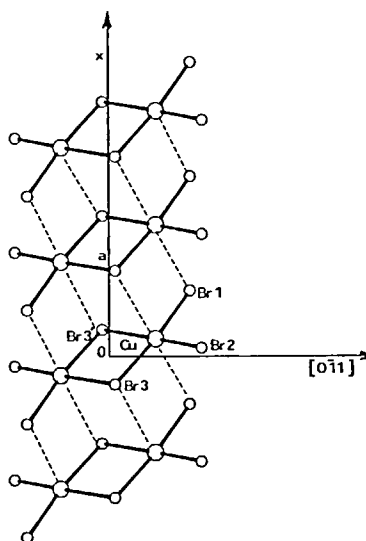


FIGURE 2 Elements of the infinite chain of $\text{Cu}_2\text{Br}_6^{2-}$ dimeric units in the crystal lattice of $(4,4'\text{-bipyH}_2)\text{Cu}_2\text{Br}_6$.

ling scheme and packing of the ions in the unit cell. Selected bond lengths and angles are given in Table II. The stacking of planar $(4,4'\text{-bipyH}_2)^{2+}$ and nearly planar centrosymmetric $\text{Cu}_2\text{Br}_6^{2-}$ ions forms cationic and anionic columns extended along the short crystallographic a axis. Figure 2 shows the distorted octahedral Cu(II) coordination formed by the two bridging and two terminal bromide atoms of the $\text{Cu}_2\text{Br}_6^{2-}$ anion, and the two semicoordinate Cu-Br bonds formed by the bridging bromide atom from an adjacent dimer and the terminal bromide atom from another dimer. In the notation recently introduced for the stacking of $\text{Cu}_n\text{X}_{2n+2}$ oligomers⁹ it is $2(1/2, 1/2)$. In the dimeric $\text{Cu}_2\text{Br}_6^{2-}$ anion the Cu(II) coordination geometry is not ideally planar (the distance of the Cu atom from the best fit plane of the four Br atoms is $0.0903(6)\text{\AA}$, and the distances of Br atoms are from $0.0107(5)$ to $0.0129(6)\text{\AA}$. The bridging Cu-Br distances (average $2.453(10)\text{\AA}$) are elongated with respect to the terminal distances (average $2.382(7)\text{\AA}$), as anticipated. Cu-Br distances are about 0.11\AA longer than the corresponding Cu-Cl distances in the isostructural chlorocuprate dimer.¹ It is less than the difference in ionic radii of the two halide ions (1.95\AA , Br and 1.80\AA , Cl). The bridge Cu-Br-Cu angle of $96.28(2)^\circ$ is less than that ($100.1(4)^\circ$) in the $\text{Cu}_2\text{Cl}_6^{2-}$ dimer.¹ The Cu-Cu' distance of $3.6529(7)\text{\AA}$ is intermediate between that of the Cu-Cu' distance of $3.616(6)$ in the $\text{Cu}_2\text{Cl}_6^{2-}$ dimer¹ and $3.683(2)$ in the $\text{Cu}_2\text{Br}_6^{2-}$ ion.¹⁰ The semicoordinate Cu-Br bonds of $3.1991(7)$ and $3.3620(7)\text{\AA}$ are only about 0.05\AA longer than related interactions in the chloride crystals. Similarly, as in the chloride crystals, the negative charge is displaced from anionic columns to cationic ones by bifurcated hydrogen bonds. The observed $\text{NH}\cdots\text{Br}$ (1) and $\text{NH}\cdots\text{Br}$ (2) distances are 2.57 and 2.45\AA . In the investigated structure, shortened C-C distances in the cationic columns are not observed, but a slightly shortened Van der Waals contact between anionic and cationic columns is noted ($\text{H}(4)\cdots\text{Br}(3') = 2.80\text{\AA}$). In the complex $(4,4'\text{-bipyH}_2)\text{Cu}_2\text{Br}_6$, the $[\text{CuBr}_6]$ octahedrons are elongated along the pseudotetragonal axis and ${}^2\text{B}_{1g}$ is the ground term.

The reflectance spectra display five bands at 37700, 29400, 23530, 19230 and 12750 cm^{-1} . In the area of the electronic spectrum corresponding to the d-d transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$, only one broad band is observed, whose maximum is at about 12750 cm^{-1} . The next higher energetic band at 19230 cm^{-1} is associated with the molecular orbitals of the dimeric $\text{Cu}_2\text{Br}_6^{2-}$ species, *i.e.*, ${}^3B_{1g}$ and ${}^3B_{2u}$, and arises primarily from the in-plane π -bonding levels.¹¹ The subsequent bands correspond to charge-transfer transitions arising from π -antibonding and π -bonding orbitals.

The X-band ($\nu = 10.47$ GHz) EPR spectrum of the complex displayed only weak resonance absorption at room temperature. The observed line is typical for polymeric copper(II) systems: very broad ($\delta H_{pp} = 600$ Oe) and centred at a spectroscopic splitting factor of $g = 2.08$. With lower temperature the signal disappeared and an impurity signal ($g = 2.08_2$) was observed.

Magnetic measurements of the complex revealed magnetic susceptibility characteristic of molecular antiferromagnetics. Starting with a room temperature value of $\chi_{\text{Cu}} = 785 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, lowering the temperature led to an increase of the magnetic susceptibility to a value of $806 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ at 220 K, *i.e.*, to a value corresponding to the maximum on the curve (Fig. 3). Further temperature decrease results in a corresponding decrease of the magnetic susceptibility to the minimum at *ca* 40 K. The increased susceptibility at the lowest temperature that could be reached is indicative of a small amount of a paramagnetic copper(II) impurity. The magnetic moment of the complex (calculated per copper ion) at the room temperature is much lower than the pure spin value for the copper(II) ion (1.36 B.M.). It decreases to 0.11 B.M. at 4.2 K.

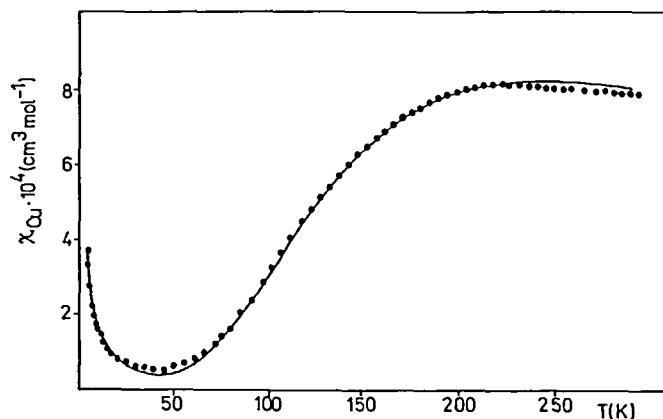


FIGURE 3 Experimental magnetic susceptibility χ_{Cu} (○) vs temperature for $(4,4'\text{-bipyH}_2)\text{Cu}_2\text{Br}_6$. The solid line was generated from a least-squares fit to the modified Bleaney-Bower's equation (1) with best-fit parameter $J = -138 \text{ cm}^{-1}$ and 0.39% monomeric impurities.

The variation of χ_{Cu} with temperature was fitted to equation (1) in the H.D.V.V. model for the interaction between two copper(II) centres,¹²

$$\chi_{\text{Cu}} = \frac{N\beta^2 g^2}{3kT} [1 + 1/3 \exp(-2J/kT)]^{-1} (1 - \rho) + \left(\frac{N\beta^2 g^2}{4kT} \right) \rho + Na \quad (1)$$

where J is the intradimer exchange parameter, ρ is the molecular weight of the

impurity and the other symbols have their usual meanings. The spectroscopic splitting factor g as determined by EPR spectroscopy at room temperature was introduced into equation (1). The J and ρ parameters were determined by searching

for the minimum of $R = \sum_{i=1}^n (X_{\text{Cu}}^{\text{exptl}} - X_{\text{Cu}}^{\text{calcd}})^2$. These parameters were found to be

$J = -138 \text{ cm}^{-1}$ and $\rho = 0.0039$. R is equal to 1.66×10^{-8} , in excellent agreement with the observed and calculated magnetic data.

After subtraction of the contribution of the monomeric form in the function $\chi_{\text{Cu}} = f(T)$, the susceptibility curve of the complex was approximated to the Bleaney-Bowers model with molecular field correction.¹³ The magnetic susceptibility data fitted to this model gave the results: intradimer exchange parameter $J = -135 \text{ cm}^{-1}$, interdimer parameter $J' = -15.6 \text{ cm}^{-1}$ and $R = 5.75 \times 10^{-9}$.

A better model for magnetic interaction in the $\text{Cu}_2\text{Br}_6^{2-}$ dimeric units should be the molecular field Heisenberg model.^{13,14} A fragment of the lattice with the four interacting magnetic copper centres is presented in Figure 4.

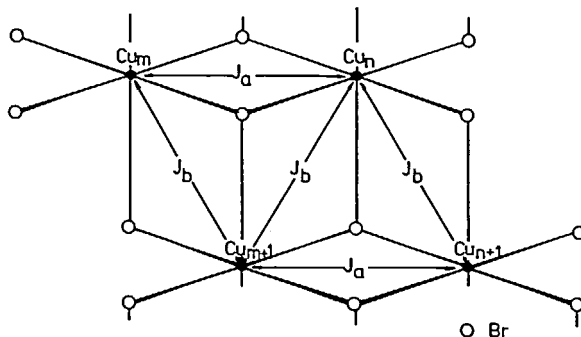


FIGURE 4 Fragment of the lattice showing the four interacting magnetic copper centres.

The Hamiltonian for a pair of spins, S_m and S_n , is given by

$$H = -2J_a S_m \cdot S_n - g\beta(S_m + S_n) \cdot H - g\beta(S_m \cdot H_m^M + S_n \cdot H_n^M)$$

where H is the external magnetic field and H_m^M is the mean internal field acting on the spin S_m . The susceptibility for the molecular field Heisenberg model can be presented as

$$\chi_{\text{Cu}} = \frac{N\beta^2 g^2}{kT(3 + e^{-2J_a/kT}) - 4zJ_b} \quad (2)$$

where $z = 2$. For this model, the best agreement was obtained for the parameters $J_a = -135 \text{ cm}^{-1}$, $J_b = -11.2 \text{ cm}^{-1}$, and standard deviation 5.75×10^{-9} . Compared with the previously studied $(4,4'\text{-bipyH}_2)\text{Cu}_2\text{Cl}_6$ complex,⁵ the J_a parameter is twice as high, and the J_b parameter much higher.

Compounds with the $\text{Cu}_2\text{X}_6^{2-}$ ($X = \text{Cl}, \text{Br}$) anionic system has been studied in detail by Willett, and other authors.¹⁵⁻²² Geiser and Willett²³ have described the

distortions of the $\text{Cu}_2\text{X}_6^{2-}$ dimer from planar coordination geometry around the Cu(II) ion, in terms of a twist angle τ between the bridging Cu_2X_2 plane and the terminal CuX_2 plane, and by bifolded or "sedia" distortion characterized by a bifold angle δ between the central Cu_2X_4 plane and the terminal CuX_3 plane. The magnetic superexchange effect in such systems is a function of three parameters $J(\varphi, \tau, \delta)$ where φ is the Cu–X–Cu bridging angle. In the studied complex the dimers aggregate in stacks and exhibit sedia distortion with $\delta = 2.89(2)^\circ$.

The results of our studies compared with others are listed in Table III. The exchange parameters calculated for the $(4,4'\text{-bipyH}_2)\text{Cu}_2\text{Br}_6$ complex seem to be high, especially as the J_b value greatly exceeds the expected one. The J_b parameter seems to point to a strong magnetic coupling of the copper centres deriving from the adjacent dimers in the chain of $\text{Cu}_2\text{Br}_6^{2-}$ units.

TABLE III
Structural and magnetic parameters of stacked planar $\text{Cu}_2\text{Br}_6^{2-}$ dimers.*

Cation	Bridging angle φ ($^\circ$)	Cu–Br bridging (Å)	J/k (K)	σ
2-amino-3-hydroxy-pyridinium ⁺	97.0	2.460		6.3
4,4'-bipyH ₂ ²⁺	96.28 ^b	2.453 ^b	–194 ^b	2.9 ^b
CH ₂ OHCH ₂ NH ₃ ⁺	95.7	2.456	–60	14.9
Melaminium ²⁺	95.6	2.468	–113	7.5
Me ₄ enH ₂ ²⁺	95.7	2.451	–134	17.5
(CH ₃) ₂ CHNH ₃ ⁺	95.1	2.446	–90	18.3

* Data from R. Willett *et al.*,¹⁸ and references therein; ^b this work.

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