

The analysis has shown that the small differences between the stabilization energies along a column arise from large cancellations of effects of similar order of magnitude. We should also point out that the values of the various components depend critically on the geometry of the cation. Solvation will certainly change the geometry of the cation, and thus also the values of the various components, so that also the overall preference might change.

Thus it can be expected that solvation might change the trend of the SE values along a column, while along a row the change is less likely.

Registry No. H_2^+CNH_2 , 54088-53-8; H_2^+COH , 17691-31-5; H_2^+CF , 35310-31-7; H_2^+CPH_2 , 84005-10-7; H_2^+CSH , 20879-50-9; H_2^+CCl , 59000-00-9.

Ab Initio Molecular Orbital Study of the CH_3N^{2+} Potential Energy Surface[†]

Wolfram Koch, Nikolaus Heinrich, and Helmut Schwarz*

Contribution from the Institut für Organische Chemie der Technischen Universität Berlin, Juni 135, D-1000 Berlin 12, West Germany. Received January 13, 1986

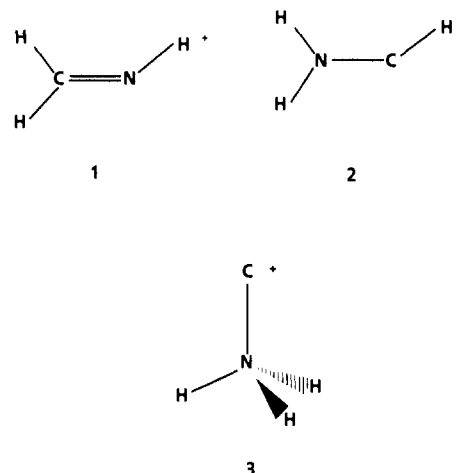
Abstract: High level MP4/6-311G(d,p)//6-31G(d)+ZPVE ab initio MO calculations predict two stable CH_3N^{2+} isomers; the global minimum corresponds to the aminomethylene dication, $\text{H}_2\text{NCH}_2^{2+}$ (**5**), which at the highest level of theory is predicted to be 49 kcal/mol more stable than H_3NC^{2+} (**6**), which can be viewed as a donor/acceptor molecule. Both isomerization and dissociation pathways were studied, and the two isomers are prevented by significant barriers from isomerization as well as dissociation (charge separation). Vertical and adiabatic ionization energies for removing an electron from the corresponding, as yet unknown, monocations are estimated as are the heats of formation of the resulting dictations. For **5**, ΔH_f° is estimated to 644 kcal/mol, and for **6** a value of 700 kcal/mol has been obtained.

The remarkable chemistry and physics of multiply charged, gaseous cations is of considerable interest to both experimentalists and theoreticians.¹ Salient features of the dications which can be conveniently generated from monocations in the gas phase by charge stripping (CS) mass spectrometry² are the following ones: (1) reversal of stability order of dicationic isomers when compared with their mono-charged or neutral counterparts; (ii) significant structural changes which often favor anti-van't Hoff geometries for the dications;³ and (iii) highly exothermic charge separation reactions which in the gas phase, however, are prevented by significant barriers to occur spontaneously. Thus, observation of the intrinsically thermochemically unstable dications is feasible, while in solution proton transfer to the solvent shell or transfer of negatively charged species to the dication will take place with avidity thus making it unlikely to generate under these conditions *small* organic dications as viable species. Larger organic dications or species which are stabilized intramolecularly can, of course, be generated as stable systems in solution.⁴

High-level ab initio molecular orbital (MO) calculations play a decisive role in the description and characterization of the species of interest in that they not only allow comparison of theoretically predicted and experimentally evaluated ionization energies but also provide information on the energetics of the ions, their electronic structures and their isomerization/dissociation characteristics.

While the potential energy surface of the CH_3N^{2+} system, which is believed to play an important role in the interstellar production of organic molecules,⁵ is now quite well understood,⁶ to the best of our knowledge no high-level ab initio MO calculations have been reported on the corresponding dicationic CH_3N^{2+} system, which is the subject of the present paper. For the monocations the aminomethylene cation (**2**) is predicted to be 8.8 kcal/mol (MP2/6-31G(d)//4-31G) more stable than the methyleneimine radical cation (**1**) (Chart I). A high-energy barrier (57 kcal/mol (MP2/6-31G(d)//4-31G)) for the reaction **1** \rightarrow **2** largely prevents the two ions from isomerizing prior to the microsecond frag-

Chart I



mentation. A third isomer **3**, which was not included in the earlier publications,⁶ is calculated to lie 60.5 kcal/mol (MP4/6-311G-

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[†] Dedicated to Professor Edgar Heilbronner, Basel, on the occasion of his 65th birthday.

Table I. Total Energies (hartrees), Relative Energies (kcal/mol), and ZPVE (kcal/mol) for CH₃N²⁺ and CH₃N⁺ Species as well as Some Dissociation Products^a

molecule	symmetry	6-31G (d)	6-311G (d,p)	MP2/6-311G (d,p)	MP3/6-311G (d,p)	MP4/6-311G (d,p)	ZPVE	E _{rel}
H ₂ CNH ²⁺ (4)	C _{2v}	-93.001 54	-93.031 04	-93.300 33	-93.316 21	-93.340 22	18.1	45.8
H ₂ CNH ⁺ (1)	C _s	-93.717 48	-93.744 57	-94.008 12	-94.029 68	-94.044 81	22.3	
H ₂ NCH ²⁺ (vert)	C _s		-92.998 64	-93.259 21	-93.277 78	-93.301 70		
H ₂ NCH ⁺ (5)	C _{2v}	-93.084 46	-93.115 04	-93.386 97	-93.400 67	-93.418 18	21.2	0.0
H ₂ NCH ²⁺ (2)	C _s	-93.725 39	-93.754 12	-94.026 01	-94.043 54	-94.057 99	24.1	
H ₂ NCH ⁺ (vert)	C _s		-93.059 52	-93.336 38	-93.349 88	-93.369 68		
CNH ₃ ²⁺ (6)	C _{3v}	-93.017 28	-93.047 90	-93.301 74	-93.325 75	-93.341 21	21.9	49.0
CNH ₃ ⁺ (3)	C ₁	-93.634 91	-93.665 45	-93.921 80	-93.945 53	-93.958 62	22.3	
CNH ₃ ²⁺ (vert)	C ₁		-93.038 43	-93.290 94	-93.316 53	-93.332 35		
TS8 (5 → 6)	C _s	-92.946 35	-92.981 47	-93.258 43	-93.276 21	-93.294 80	18.1	74.3
TS9 (5 → 4)	C _s	-93.001 31	-93.031 51	-93.304 87	-93.319 54	-93.343 53	17.8	43.8
HCNH...H ²⁺ (TS10)	C _{2v}	-93.001 33	-93.027 73	-93.316 98	-93.321 65	-93.343 66	16.8	42.3
H ₂ NC...H ²⁺ (TS11)	C _{2v}	-92.975 91	-93.003 30	-93.273 61	-93.289 02	-93.306 53	16.4	65.2
H ₂ N...CH ²⁺ (TS12)	C _s	-92.861 98	-92.891 25	-93.109 07	-93.142 41	-93.157 40	19.3	161.6
CNH ₂ ...H ²⁺ (TS13)	C _s	-92.929 30	-92.955 15	-93.221 43	-93.238 45	-93.256 15	16.5	96.9
C...NH ₃ ²⁺ (TS14)	C _s	-92.956 42	-92.971 71	-93.225 51	-93.252 26	-93.272 65	21.8	91.9
HNCH ⁺	C _s	-93.159 04	-93.185 97	-93.477 78	-93.482 61	-93.503 42	17.2	
CNH ₂ ⁺	C _{2v}	-93.092 83	-93.119 61	-93.386 01	-93.403 67	-93.420 38	15.8	
HC ⁺	C _{∞v}	-37.895 54	-37.904 51	-37.977 55	-37.996 73	-38.003 65	4.6	
NH ₂ ⁺ (singlet)	C _{2v}	-55.127 29	-55.149 35	-55.278 72	-55.298 03	-55.303 90	10.9	
NH ₂ ⁺ (triplet)	C _{2v}	-55.208 52	-55.230 66	-55.340 25	-55.355 65	-55.359 55	10.4	
NH ₃ ⁺	D _{3h}	-55.873 24	-55.898 00	-56.048 81	-56.064 92	-56.069 87	19.8	
C ⁺ (2p)	K _h	-37.287 07	-37.291 80	-37.336 54	-37.351 87	-37.358 02		

^aSome data for the cationic reference compounds were taken from the following: Whiteside, R. A.; Frisch, M. J.; Pople, J. A., The Carnegie Mellon Quantum Chemistry Archive, 3rd Edition, Pittsburgh, PA, 1983.

(d,p)//6-31G(d)) above 2. What the situation looks like, when an additional electron is removed from 1 and 2, has been evaluated by high-level ab initio MO calculations, and likely features of CS experiments are predicted.

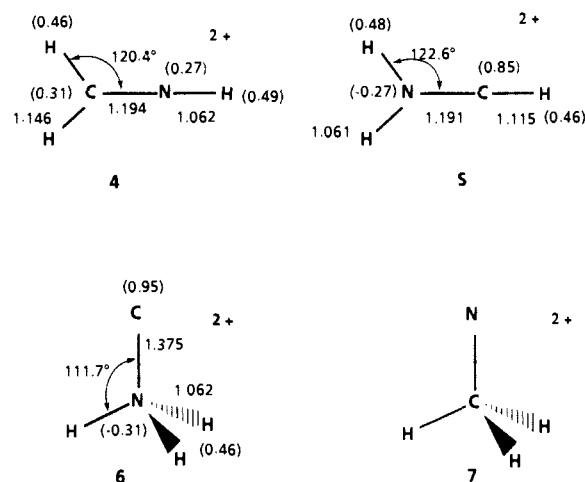
Method

Standard ab initio MO calculations were carried out with use of the CRAY version of the GAUSSIAN 82 series of programmes.⁷ Optimized geometries, harmonic frequencies, and zero-point vibrational energies were calculated with the 6-31G(d) basis set,⁸ whereas single-point calculations on the optimized geometries were performed with the d,p-polarized 6-311G(d,p) basis set⁹ which is of triple valence quality. Open-shell systems were treated with the unrestricted HF (UHF) formalism.¹⁰ Effects of valence electron correlation were incorporated by means of Møller-Plesset perturbation theory up to full fourth order.¹¹ This level of theory, which is used throughout in the paper if not stated otherwise, will be referred to as MP4/6-311G(d,p)//6-31G(d).

Results and Discussion

Optimized 6-31G(d) structures (bond length in Å, bond angle in deg) are displayed in Chart II; charges, which were obtained at the 6-311G(d,p) level by means of Mulliken population analysis, are given in parentheses. Energies (total energies in hartrees, relative energies, E_{rel}, and zero-point vibrational energy (ZPVE), scaled by a factor of 0.9 to account for the overestimation of harmonic frequencies at that level of theory,¹² are given in kcal/mol) obtained at the various levels of theory are given in Table I. Energies discussed in the text refer to the MP4/6-

Chart II



31G(d,p)//6-31(d)+ZPVE and structural parameters to the 6-31G(d) values. In Table I we also include some data of mono-charged CH₃N⁺ isomers pertinent to the discussion of vertical and adiabatic energies for the respective mono-cations. Also included in Table I are energies of transition states for both isomerization and dissociation processes of CH₃N²⁺ together with data for the relevant products.

Among the four possible isomers of CH₃N²⁺, we have located species 4, 5, and 6 as minima. The fourth isomer, CH₃N²⁺ (7), does not correspond to a minimum; upon geometry optimization 7 falls apart into H₂ and HCN²⁺. The global minimum on the potential energy surface corresponds to the aminoethylene dication (5), which at the highest level of theory is found to be 45.8 kcal/mol more stable than the conventional methyleneimine dication (4). Thus, in the case of the CH₃N⁺/CH₃N²⁺ systems removal of an electron does not result in a reversal of stability order but rather increases the difference (compare the 8.3-kcal/mol difference for the 1-2 pair with 45.8 kcal/mol for the dicationic 4-5 system). One possible reason for the increased stability of 5 over 4 may be found in the charge distribution of the dications. While most of the charge in all small dications is, for electrostatic reasons, invariably deflected to the hydrogen periphery, 5 is additionally stabilized over 4 by Coulomb attraction

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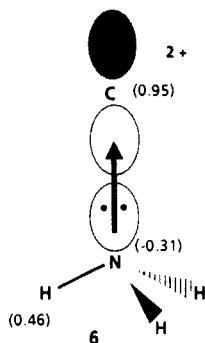
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Chart III

Table II. Calculated Vertical and Adiabatic Ionization Energies (in eV) of CH₃N²⁺ Isomers

CH ₃ N ²⁺ isomers	IE _v	IE _{ad}
CH ₂ NH ²⁺ (1)	20.2	
CHNH ₂ ²⁺ (2)	18.7	17.3
CNH ₃ ²⁺ (3)	17.0	16.8

between the HNC unit due to charge alternation; **4**, however, lacks this special stabilization. Common to both dications is the surprisingly short C–N bond length (1.194 Å for **4** and 1.191 Å for **5**) which is significantly shorter than that for the respective mono-charged radical ions **1** and **2** (**1**, 1.243 Å; **2**, 1.251 Å). In terms of valence bond structures, the bond shortening could be due to structures like H₂C=N²⁺H (for **4**) and H₂N⁺=C⁺H (**5**) which, again, would energetically favor **5** over **4**. Only 3.2 kcal/mol less stable than **4** is the dication **6** which can be viewed as a donor/acceptor molecule between NH₃ and C²⁺(1S) (Chart III).

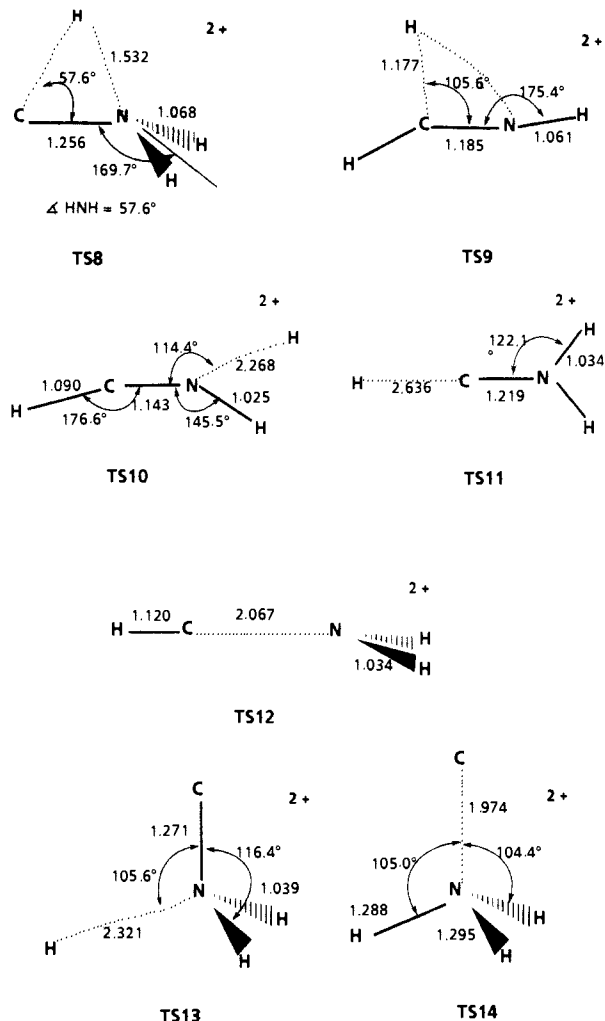
Quite surprisingly, the NH₃ fragment of **6** has retained several structural features of the uncomplexed NH₃. For example, the overall symmetry is unchanged whereas the XNH angle is only slightly changed (NH₃; ∠XNH = 111.6°; **6**, 117.7°), and the NH distance of free NH₃ (*d*_{NH} = 1.002 Å) is elongated to 1.062 Å in **6**. The charge distribution of **6** points to a formal charge transfer of 1.05 electrons from the lone pair of NH₃ to the empty p_z orbital of C²⁺, resulting in a CN bond the bond length of which is 1.375 Å, in between a CN single (ca. 1.47 Å) and CN double bond (ca. 1.30 Å). Again, one reason for the short CN bond of **6** may be found in the Coulomb attraction between the two heavy atoms.

The instability of **7** can be explained by comparing the relevant VB structures of **6** and **7**. While in **6** the two positive charges are located on two different centers, i.e., H₃N⁺–C⁺, this is not possible in **7**, i.e., H₃C–N²⁺. As a consequence, the extremely electron deficient nitrogen in **7** will attract electron density from the CH₃ bonding orbitals, resulting in a weakening of these bonds, which finally leads to dissociation. Geometry optimization of **7** under the constraint of C_{3v} symmetry (to prevent dissociation) leads to a structure (which is, of course, artificial and without any chemical relevance) which is 134 kcal/mol less stable than **5** (6-31G(d)). This result also points to the extreme *thermodynamic* instability of this structural arrangement.

From the data presented in Table I both the vertical (IE_v) and adiabatic ionization energies (IE_{ad}) for removing an electron from **1**, **2**, and **3** can be evaluated. The data are given in Table II and should guide experimentalists to perform charge stripping experiments. As both ions **5** and **6**—but not **7**, as shown below—reside in deep potential wells, these novel dications should, in principle, be accessible in gas-phase experiments by using CS. **4**, however, if generated via vertical electron loss from **1**, is predicted to rearrange spontaneously to **5**.

For further characterization of the CH₃N²⁺ potential energy surface we have performed various calculations for both isomerization and dissociation processes. For the isomerization **5** → **6**, via transition state TS8, we obtain a barrier of 74.3 kcal/mol which leaves no doubt that both isomers once generated will not

Chart IV



spontaneously interconvert. The location of the transition state connecting **5** with **4**, via TS9, caused some problems. At the 6-31G(d) level TS9 was found to be only 0.1 kcal/mol less stable than **4**. If one includes the effects of correlation energy and ZPVE, the 0.1-kcal/mol barrier for the reaction **4** → **5** disappears, in other words, at the highest level of theory CH₂NH²⁺ (**4**) cannot be regarded as a stable species but rather rearranges to CHNH₂²⁺ (**5**). This behavior is somewhat reminiscent of that for the C₂H₃⁺ system, which is isoelectronic with CH₃N²⁺, and for which it was observed that the barrier for the degenerate 1,2-hydrogen migration completely disappears at a higher level of theory thus leaving the bridged C₂H₃⁺ as the only minimum.¹³

For the remaining CH₃N²⁺ isomers **5** and **6** we have investigated several charge separation processes (eq 1–5) involving the transition states TS10–TS14. Although most of these charge separation processes are (not unexpected) exothermic, they are nevertheless characterized by substantial barriers thus preventing spontaneous dissociation to mono-charged species. While the

	ΔH_r° (kcal/mol)	E_a
HCNH ₂ ²⁺ (5) $\xrightarrow{\text{TS10}}$ HCNH ⁺ + H ⁺	-57.5	42.3 (1)
HCNH ₂ ²⁺ (5) $\xrightarrow{\text{TS11}}$ CNH ₂ ⁺ + H ⁺	-6.8	65.2 (2)
HCNH ₂ ²⁺ (5) $\xrightarrow{\text{TS12}}$ HC ⁺ + NH ₂ ⁺ (S)	+63.7	161.6 (3)
	+34.5	
CNH ₃ ²⁺ (6) $\xrightarrow{\text{TS13}}$ CNH ₂ ⁺ + H ⁺	-55.7	47.8 (4)
CNH ₃ ²⁺ (6) $\xrightarrow{\text{TS14}}$ C ⁺ + NH ₃ ⁺	-56.4	42.8 (5)

calculated barriers for processes 1–4 are likely to be correct, this must not be the case for reaction 5 which is associated with a

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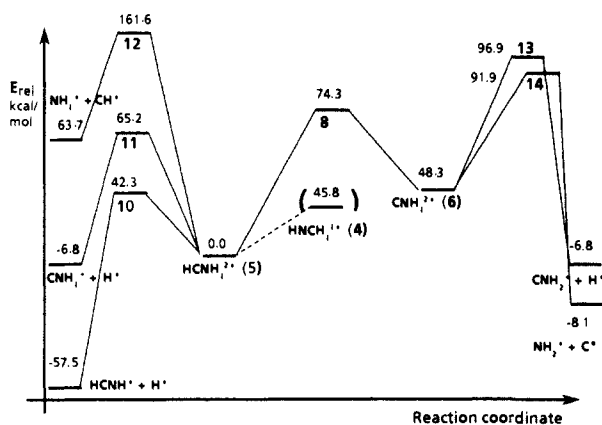


Figure 1. Potential energy diagram for CH₃N²⁺ isomers. Relative energies (referred to the energy of H₂NCH₂²⁺ (5)) are given in kcal/mol. The reaction co-ordinate is a complex co-ordinate.

transition state of singlet diradicaloid character. As the UHF method (which has been used to localize this saddle point) is known for its poor description of singlet diradicals, the energy of TS14 is likely to be too high. But, ion 6 also seems to be prevented by

significant barriers from spontaneous dissociation. In Figure 1 the various isomerization/dissociation processes are given in a simplified two-dimensional potential energy surface.

Heats of formation ΔH_f⁰, of 5 and 6 can be estimated from combining the ΔH⁰, of reactions 1-5 with the experimentally determined heats of formation of the various mono-cations;¹⁴ by doing this, for H₂NCH₂²⁺ (5) an averaged value of ΔH_f⁰ = 644 kcal/mol and for H₃NC²⁺ (6) of ΔH_f⁰ = 700 kcal/mol is obtained. Both numbers indicate the extreme thermodynamic instability of the two dications, and it is highly unlikely to ever generate a stable CH₃N²⁺ species in solution. Proton transfer to the solvent shell or capture of negatively charged species from it will occur with avidity.

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Nonempirical Valence Bond Studies of the Origin of the Antiferromagnetism of Copper(II) Carboxylate Dimers

Richard D. Harcourt,*† Frances L. Skrezenek,† and Robert G. A. R. MacLagan†

Contribution from the Department of Physical Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia, and the Department of Chemistry, University of Canterbury, Christchurch 1, New Zealand. Received February 18, 1986

Abstract: The origin of the antiferromagnetism of copper(II) carboxylate dimers is examined by using nonempirical valence bond procedures to calculate values for $-2J = E_{\text{triplet}} - E_{\text{singlet}}$, in which J is the magnetic exchange parameter. Ten electrons and six atomic orbitals are explicitly included in the calculations. The orbitals consist of the copper $d_{x^2-y^2}$ and a lone-pair $2p\pi$ orbital on each oxygen atom of two carboxylate ligands. The nearest-neighbor Cu-O overlap is essentially σ in character. The results of the calculations support a conclusion obtained from an earlier semiempirical study, namely that O-O overlap within each of the carboxylate ligands is primarily responsible for the antiferromagnetism. The O-O overlap becomes effective when the oxygen lone-pair electrons delocalize into the singly occupied $d_{x^2-y^2}$ orbitals and leads to appreciable stabilization of the $S = 0$ state via covalent-ionic resonance. For $-2J \approx 300 \text{ cm}^{-1}$, the primary covalent and ionic structures for this purpose involve three $2p\pi$ -electrons within either or both carboxylate ligands. The resulting covalent-ionic resonance leads to the development of a Pauling "3-electron bond", $\text{O} \cdots \text{O}(\equiv \text{O} : \text{O} \leftrightarrow \text{O} : \text{O})$ within a carboxylate ligand.

The copper acetate monohydrate dimer is perhaps the best-known member of a large class of similarly structured Cu(II) carboxylate dimers with the general formula Cu₂(RCO₂)₄L_n, where $n = 0$ or 2. Each of these dimers involves two Cu²⁺ ions which are bridged symmetrically by four carboxylate ligands. It is well-known that this type of dimer involves an $S = 0$ ground state, i.e., the spins of the two magnetic electrons which originate from the (3d)⁹ configurations of the two Cu²⁺ ions are antiparallel, and a thermally accessible $S = 1$ excited state. As a result, antiferromagnetism is observed. A singlet-triplet energy separation (${}^3E - {}^1E = -2J$) of 286 cm⁻¹ has been reported^{1,2} for Cu₂(CH₃CO₂)₄ · 2H₂O, and other copper(II) carboxylate dimers have $-2J$ values of 100-550 cm⁻¹.³⁻⁷

To account for the antiferromagnetism of copper acetate, Figgis and Martin^{1,2} suggested that for the $S = 0$ ground state, a weak

Table I. Atomic Orbital Overlap Integrals

S ₁₂	0.069 41 (0.069 2) ^a	S ₁₅	0.000 07 (0.0) ^a
S ₁₃	0.000 38 (0.000 29) ^a	S ₁₆	0.000 38 (0.000 53) ^a
S ₁₄	0.019 60 (0.011 27) ^a	S ₂₃	0.001 09 (0.000 23) ^a

^aReference 15, with sp² hybridized oxygen AOs, ζ_O = 2.2266 and ζ_{Cu}(3d) = 3.080.

Cu-Cu δ-bond is formed by the lateral overlap of singly occupied 3d_{x²-y²} atomic orbitals (AOs). For this type of bond, Ross and

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*University of Melbourne.

†University of Canterbury.