

set by the addition of p-polarization functions on hydrogen decreases the magnitude of the frequency from 416 to 376 cm^{-1} . This is substantially identical with the result obtained with the polarized Dunning (9,5) double- ζ basis D95(d,p).¹¹ The addition of a third set of valence s and p functions (6-311G(d,p))¹² leads to a further decrease of 66 cm^{-1} in the vibrational frequency to 310 cm^{-1} . Neither the addition of diffuse functions (6-311++-G(d,p)),¹³ a second set of polarization functions (6-311G(2d,2p)),¹⁴ nor d functions on hydrogen (6-311G(d,pd))¹⁴ leads to a significant change in the frequency. This sequence leads us to conclude that, at the basis set limit, H_2CN^+ is a relative minimum on the potential energy surface. However, at the correlated MP2 level of theory, H_2CN^+ is a saddle point on the potential surface as indicated by the imaginary frequencies in Table I. Note that increasing basis set size works in the same direction at both the SCF and correlated levels. At the SCF level increasing the size of the basis decreases the magnitude of the real frequency whereas at the MP2 level it increases the magnitude of the imaginary frequency, making it likely that even larger basis sets would favor the conclusion that C-protonated HCN is at a saddle point rather than at a minimum. Configuration interaction frequencies including all double excitations (CID is correct to third order in the perturbation theory expansion¹⁵) were computed with the 6-31G(d,p) basis. As with geometries,¹⁶ MP2 overestimates the correlation correction to the vibrational frequency and the CID answer lies between the SCF and MP2 values and is imaginary by a significant magnitude.

The possibility that higher order correlation terms would change the conclusion that H_2CN^+ is at a saddle point is negligible, and even if they did the barrier to isomerization to the linear isomer would be too small to allow detection of the C-protonated isomer. (At the MP2/6-311++G(d,p) level of theory the vertical charge reversal reaction leaves H_2CN^+ excited by 5 kcal mol^{-1} .) A possible explanation for the collisional activation results is that the charge-reversal reaction produces an excited-state triplet species. It has been shown theoretically¹ that the H_2CN^+ structure is a stable minimum on the triplet potential energy surface and that it is $\sim 120 \text{ kcal mol}^{-1}$ above the linear singlet structure. Furthermore, there is precedent for the production of electronically excited cations by the charge reversal reaction.¹⁷ Indeed, the production of triplet methoxy cations, H_3CO^+ , from methoxide^{17b} provides a close analogy as singlet H_3CO^+ is not a stable minimum on the CH_3O^+ potential surface.

The qualitative similarities between the CH_2N^{+1} system and the $\text{C}_2\text{H}_4\text{N}^{+18}$ system should be noted here. Both hydrogen cyanide and methyl cyanide protonate only on the terminal nitrogen atom and not on the nitrile carbon. The only stable isomer of $\text{C}_2\text{H}_4\text{N}^+$ corresponding to protonated CH_3CN is CH_3CNH^+ ; the C-protonated form is a saddle point on the potential energy surface as is the C-protonated form of HCN considered in this paper. By contrast, hydrogen isocyanide and methyl isocyanide both have stable protonated isomers resulting from protonation at either the terminal carbon or the isonitrile nitrogen.

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Unprecedented C-N Bond Formation. Crystal and Molecular Structure of *N*-(2-Aminoethyl)-*N*-(4-aza-6-aminohexyl)-(α,α -diaminomalonato)cobalt(III) Perchlorate

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We wish to report on a novel compound unexpectedly obtained from the reaction of α -aminomalonate (AM^{2-}) with *trans*- $[\text{CoCl}_2(2,3,2\text{-tet}^3)]\text{ClO}_4$.

In our laboratory, asymmetric decarboxylations of α -amino- α -alkylmalonates (ARM^{2-}) using a chiral cobalt(III) complex containing an optical active tetraamine have been investigated.⁴ Every X-ray study of some stereospecifically obtained α -amino- α -methylmalonate (AMM) complexes containing optical active tetraamines revealed⁵ that the AMM ion coordinates to the central metal through the amino group and through one of the carboxyl groups in the *cis*- β_2 fashion, and the uncoordinated carboxyl group forms the intramolecular hydrogen bond to one of the secondary nitrogens of the tetraamine. As a continuation of our research on the series of the ARM complexes, we have recently used AM , which has an active proton in place of the alkyl group, and have tried to prepare its cobalt(III) complex with 2,3,2-tet.⁶

Contrary to our expectation from the AMM complexes, a novel compound containing a geminal diamine linkage as a result of an unexpected bond formation between the α -carbon of the AM moiety and one of the secondary nitrogens of the tetraamine was obtained and characterized by X-ray crystallography.

The complex was prepared by the same procedure as has been employed in the preparation of the ARM complexes; *trans*- $[\text{CoCl}_2(2,3,2\text{-tet})]\text{ClO}_4$ and ammonium α -aminomalonate were refluxed for 3 h in absolute methanol in the presence of triethylamine. After the solvent had been removed, the residue was dissolved in water and subjected to SP-Sephadex C-25 column chromatography. Elution with 0.01 N NaClO_4 produced an orange band, which is supposed to be singly charged, as the major product and a large amount of brownish species which strongly adsorbed to the resin. Concentration of the eluate yielded good orange crystals.⁷

The molecular structure of the complex established by the X-ray study⁸ is illustrated in Figure 1. The tetraamine moiety coor-

(1) The University of Tokyo.

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(3) The fully systematic name is 3,7-diaza-1,9-diaminononane.

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(6) This tetraamine was chosen because this system gave good crystals suitable for an X-ray crystallographic study. A similar product was also obtained in the system containing (4*R*,6*R*)-4,6-dimethyl-3,7-diaza-1,9-diaminononane (5*R*,7*R*- Me_2 -2,3,2-tet).

(7) Anal. ($\text{C}_{10}\text{H}_{21}\text{N}_5\text{O}_4\text{CoClO}_4$) C, H, N, Cl. ¹H NMR (D_2O) 1.95-2.35, 2.50-3.35 (complicated pattern, CH_2 of 2,3,2-tet) ppm; ¹³C NMR (D_2O) 24.6, 44.8, 45.2, 47.1, 48.8, 51.2, and 57.4 (t, CH_2 of 2,3,2-tet), 85.6 (s, α -C of AM), 176.2 and 177.1 (s, COO^- of AM) ppm; AB (H_2O) ν_{max} 20 700 (log ϵ = 2.16), 28 200 (log ϵ = 2.06) cm^{-1} .

Scheme I

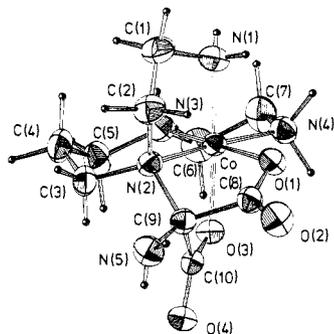
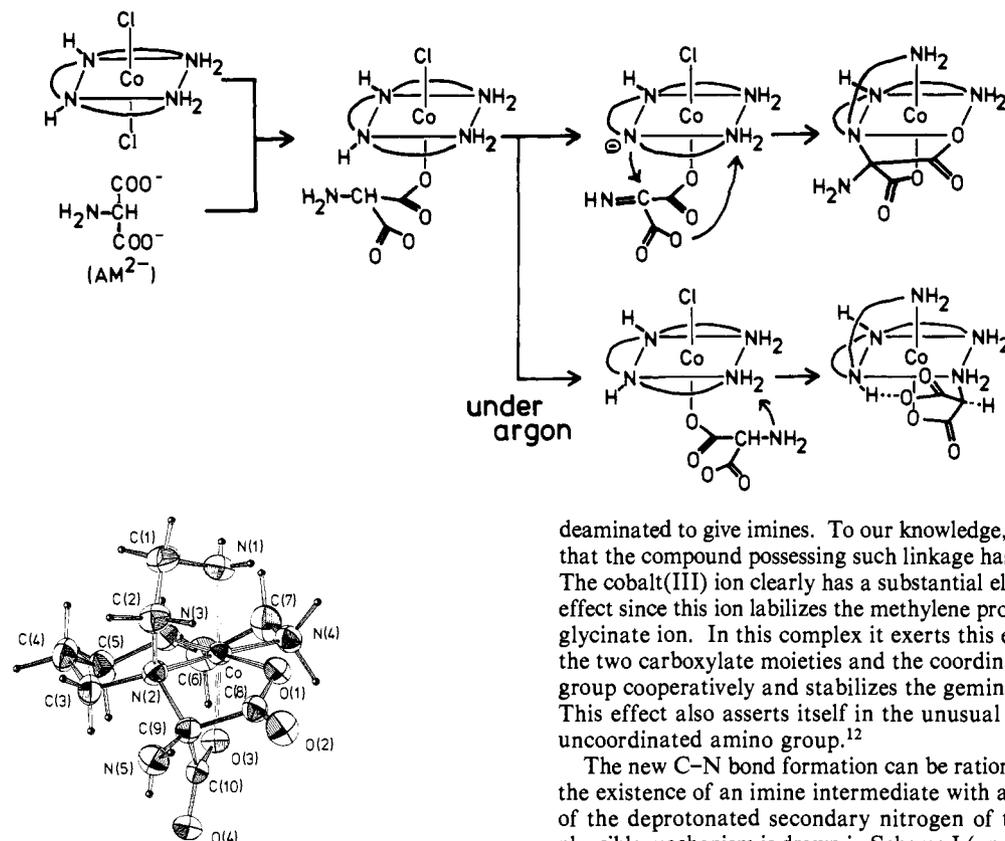


Figure 1. A perspective drawing of the complex ion and the numbering scheme for the atoms. Selected bond distances: N(2)–C(2), 1.509 (5); N(2)–C(3), 1.498 (4); N(2)–C(9), 1.528 (4); N(5)–C(9), 1.422 (5); C(8)–C(9), 1.541 (4); C(9)–C(10), 1.550 (4) Å. Angles: O(1)–Co–N(2), 84.8 (1)°; O(3)–Co–N(2), 84.2 (1)°; Co–N(2)–C(9), 96.0 (2)°; N(2)–C(9)–N(5), 113.5 (3)°; N(2)–C(9)–C(8), 105.8 (2)°; N(2)–C(9)–C(10), 102.7 (2)°; N(5)–C(9)–C(8), 115.6 (3)°; N(5)–C(9)–C(10), 113.9 (3)°; C(8)–C(9)–C(10), 104.1 (2)°.

dinates to the cobalt(III) center through the four nitrogen atoms (N(1), N(2), N(3), and N(4)) in the *cis-β* fashion. The AM moiety coordinates through the two oxygen atoms (O(1) and O(3)) of the two carboxyl groups, but the amino group (N(5)) doesn't participate in coordination.⁹ The α -carbon of the AM moiety (C(9)) surprisingly links to the secondary nitrogen (N(2)) of the tetraamine with the distance of 1.528 (4) Å, which is longer than the usual values for the C–N bond.⁹ In contrast, the N(5)–C(9) distance is shorter (1.422 (5) Å) than the usual values.¹⁰

The most remarkable feature of this complex is the unusual stability of the geminal diamine linkage (N(2)–C(9)–N(5)) containing a primary nitrogen (N(5)). This type of linkage could be assumed in the unstable intermediate formed in the reaction of imines with other amines.¹¹ The intermediate is immediately

deaminated to give imines. To our knowledge, this is the first case that the compound possessing such linkage has ever been isolated. The cobalt(III) ion clearly has a substantial electron-withdrawing effect since this ion labilizes the methylene protons of the chelated glycinate ion. In this complex it exerts this effect through both the two carboxylate moieties and the coordinated tertiary amino group cooperatively and stabilizes the geminal diamine linkage. This effect also asserts itself in the unusual low basicity of the uncoordinated amino group.¹²

The new C–N bond formation can be rationalized by assuming the existence of an imine intermediate with a subsequent attack of the deprotonated secondary nitrogen of the tetraamine. A plausible mechanism is drawn in Scheme I (upper). A comparative reaction of malonic acid (malH₂) with *trans*-[CoCl₂(2,3,2-tet)]–ClO₄ under the same condition yields an usual malonato complex¹³ [Co(mal)(2,3,2-tet)]⁺, indicating that the existence of the α -amino group is essential in the C–N bond formation. A reaction run under an atmosphere of argon yields a different complex selectively,¹⁴ in which the AM ion is believed to coordinate through the amino group and through one of the carboxyl groups in the same manner as is observed in the chelation of an AMM ion⁵ (Scheme I, lower). This observation indicates the C–N bond cannot be formed in the absence of oxygen. The presence of oxygen is probably important in the dehydrogenation process. It has been reported that RuCl₃/PR₃ catalyzes the conversion of primary amines to secondary amines.¹⁵ In the reaction, the C–N bond formation is also assumed to proceed via an initial dehydrogenation of the primary amine followed by an attack of the other amine molecule. It is striking that the AM ion is easily dehydrogenated under such mild conditions, as compared with the reported case of the dehydrogenation of primary amines.^{11,15}

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(8) Crystal data: C₁₀H₂₁CoN₅O₄ClO₄, monoclinic, space group *P*2₁/*c*, *a* = 7.399 (5) Å, *b* = 23.199 (5) Å, *c* = 9.452 (4) Å, β = 92.02 (5)°, *d*_m = 1.78, *d*_c = 1.78 g cm⁻³ for *Z* = 4. Intensity data were measured on a Rigaku automated four-circle diffractometer using graphite-monochromated Mo K α radiation at room temperature in the range $2\theta \leq 60^\circ$ ($\pm h, \pm k, \pm l$). The structure was solved by direct methods and refined by full-matrix least-squares procedures with anisotropic temperature factors for non-H atoms (hydrogen atoms isotropically) using 3712 unique reflections with $|F_o| \geq 3\sigma(F_o)$ (corrected for absorption, $\mu = 1.319$ mm⁻¹) to final *R* = 0.0497 and *R*_w = 0.0515 (weighting scheme: $w = (a|F_o|^2 + b|F_o| + c)^{-1}$, *a*, *b*, and *c* were automatically calculated). All calculations were performed on a FACOM M380 computer of the Institute of Physical and Chemical Research using the UNICS III program system. (Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, 55, 69–77).

(9) Two oxygens of perchlorate ions were observed to contact closely to N(5): N(5)···O(5)^a 3.367 (6) Å, N(5)···O(7)^b 3.290 (7) Å. Symmetric operations: (a) *x*, *y*, 1 + *z*; (b) –1 + *x*, *y*, 1 + *z*.

(10) The average value for the C–N bonds in the tetraamine moiety is 1.491 Å.

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(12) The titration curve demonstrates that the proton does not associate with p*K*_a higher than 3, while in the parent AM ion p*K*_a = 9.5.

(13) The ¹H NMR spectrum (400 MHz) reveals a characteristic AB pattern (*J* = 19.46 Hz, $\delta\nu$ = 26.9 Hz) at 3.40 ppm, which can be assigned to the nonequivalent geminal methylene protons of the malonato moiety coordinated without C–N bond formation.

(14) The product shows the proton resonance signal at 4.2 ppm, which gradually decreases by the exchange with D in D₂O. The signal can be assigned to the α -proton of the chelated AM moiety. The complex readily decarboxylates to give a glycinate complex by the reaction with HCl. These observations indicate the chelation of the AM ion without the C–N bond formation. A reaction in weak basic aqueous media (pH 8) in contact with the atmosphere also yields the same product. This complex can be a precursor in an advantageous route of the asymmetric syntheses of [2-²H₁]glycine, when it is decarboxylated in the presence of D⁺, by the application of our cyclic system for the asymmetric syntheses of α -amino acids.⁴

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Supplementary Material Available: Listings of positional and thermal parameters and mean square displacement tensors of atoms (2 pages). Ordering information is given on any current masthead page.

Hexakis(μ_3 -thio)pentakis[(η^5 -cyclopentadienyl)-titanium], [(η^5 -C₅H₅)Ti]₅(μ_3 -S)₆: Preparation and Molecular and Electronic Structure[†]

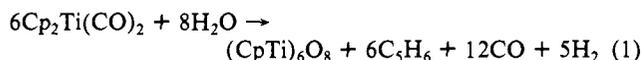
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In earlier work we have described [(CpCr)₄(μ_3 -O)₄] and [(CpV)₅(μ_3 -O)₆] (Cp = η^5 -C₅H₅),¹ which together with [(CpTi)₆(μ_3 -O)₈] described by Caulton and co-workers² provide a series of novel oxygen-containing clusters which obey Euler's theorem. A theoretical study of these clusters showed that there were 12 cluster orbitals occupied by 2 ((CpTi)₆O₈), 8 ((CpV)₅O₆), or 12 ((CpCr)₄O₄) electrons.³ According to this analysis a wide variety of more or less distorted octahedral (CpM)₆A₈, trigonal-bipyramidal (CpM)₅A₆, and tetrahedral (CpM)₄A₄ clusters (M = first-row transition metal and A = μ_3 -atom from groups 15 or 16) should be obtainable. In the tetrahedral case several thio derivatives [(CpM)₄S₄]^{m+} (M = Cr, Fe, Co) are known.⁴ We have been seeking other members of these series, particularly nontetrahedral derivatives, and report here the preparation and structure of the first trigonal-bipyramidal thio cluster, [(CpTi)₅(μ_3 -S)₆].⁵

In their report on (CpTi)₆O₈ Caulton and co-workers suggested that the cluster was actually obtained from Cp₂Ti(CO)₂ and H₂O.² We have confirmed this suggestion and find that the reaction between Cp₂Ti(CO)₂ and H₂O (3:4 mol ratio) in toluene at 80 °C is quantitative and gives (CpTi)₆O₈ as the *only* titanium-containing product according to the equation:



This remarkable specificity suggested that a similar reaction with H₂S would take place. It does, but the product is (CpTi)₅(μ_3 -S)₆ (73% yield based on the Cp₂Ti(CO)₂ used) not (CpTi)₆S₈, thus illustrating our contention that the clusters obeying Euler's theorem

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(5) [Cu₅(μ_2 -S-t-Bu)₄]⁻ contains a trigonal bipyramid of Cu atoms enclosed within an open octahedron of μ_2 -S-t-Bu ligands: Dance, I. G. *J. Chem. Soc., Chem. Commun.* **1976**, 68.

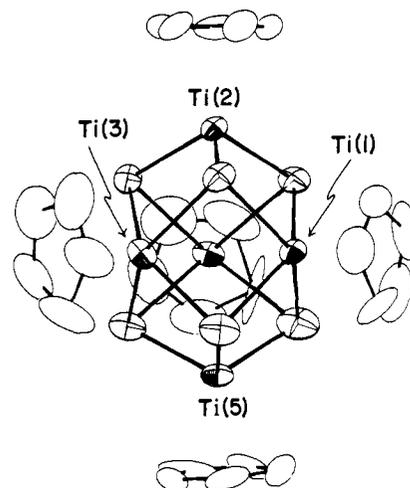


Figure 1. ORTEP drawing of (CpTi)₅S₆. Hydrogen atoms are omitted for clarity. Ti-Ti distances: Ti(1)-Ti(2) 3.152 (5); Ti(1)-Ti(3) 3.148 (5); Ti(1)-Ti(4) 3.214 (5); Ti(1)-Ti(5) 3.145 (5); Ti(2)-Ti(3) 3.173 (5); Ti(2)-Ti(4) 3.169 (5); Ti(3)-Ti(4) 3.172 (5); Ti(3)-Ti(5) 3.161 (5); Ti(4)-Ti(5) 3.076 (5) Å. Ti-S distances: Ti(1)-S(3) 2.468 (6); Ti(1)-S(4) 2.485 (7); Ti(1)-S(5) 2.480 (7); Ti(1)-S(6) 2.463 (7); Ti(2)-S(2) 2.274 (6); Ti(2)-S(3) 2.308 (6); Ti(2)-S(4) 2.277 (7); Ti(3)-S(1) 2.443 (7); Ti(3)-S(2) 2.506 (7); Ti(3)-S(3) 2.461 (6); Ti(3)-S(5) 2.444 (7); Ti(4)-S(1) 2.458 (6); Ti(4)-S(2) 2.487 (7); Ti(4)-S(4) 2.488 (6); Ti(4)-S(6) 2.504 (8); Ti(5)-S(1) 2.286 (7); Ti(5)-S(5) 2.268 (7); Ti(5)-S(6) 2.263 (8) Å.

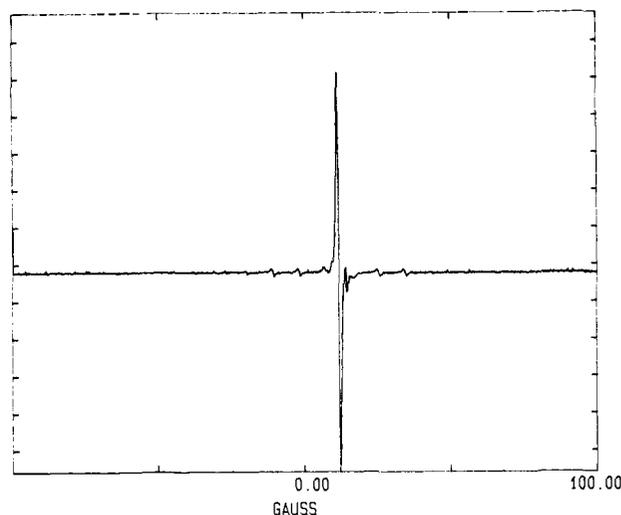
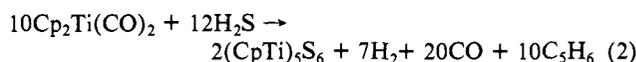


Figure 2. ESR spectrum of (CpTi)₅S₆ at 20 °C.

are closely related. Analysis of the gaseous and solid products of the reaction between Cp₂Ti(CO)₂ (6.4 mmol) and gaseous H₂S (7.7 mmol) in toluene at 80 °C for 72 h suggests that the stoichiometry of the reaction producing (CpTi)₅S₆ is



though other sulfur-containing products are obtained. The new cluster is dark green-brown, moderately air sensitive, very soluble in toluene and forms large crystals when the toluene solutions are layered with hexane.⁶

(6) Analyses of the bulk material (powder) shows it contains one molecule of toluene of crystallization per (CpTi)₅S₆ unit; this toluene is not present in the crystal examined by X-ray diffraction. Analytical results (by Beller Laboratorium, Göttingen, W. Germany) of samples from two distinct preparations: Calcd for (CpTi)₅S₆·C₆H₅CH₃ (C₃₃H₃₃S₆Ti₅): C, 45.2; H, 3.9; S, 22.6; Ti, 28.2%. Found: C, 45.7, 45.6; H, 4.2, 4.3; S, 15.2, 10.8; Ti 27.7, 28.7%. The problem of incorrect sulfur analyses in cyclopentadienyl metal complexes has been discussed by other workers.⁷