6 loses carbon monoxide, and subsequent coordination transfer gives the complex **2a,b**. Alternatively, the thioallyl cation complex **6**, on account of the strong sulfur–iron bond, prefers to eliminate the allene **5b,c** and iron-bound sulfur. In the case of the less hindered allene episulfide **1a**, this rupture of the C–S bond in **6** easily occurred to yield $S_2Fe_2(CO)_6$ (**7**) and tetramethylallene,[10d] which finally coupled to give **3**. The compound **4** is thought to come from oxidation of 2,4-dimethyl-1,3-pentadiene-3-thiol, which is formed from the thermal 1,4-hydrogen shift of **1a** via thioallyl diradical. When the more hindered allene episulfide, di-*tert*-butyldiphenylallene episulfide **1c**, was treated with diiron nonacarbonyl, no (thioallyl)iron carbonyl complex was detected; instead, isomer **1d** and 1,1-di-*tert*-butyl-3,3-diphenylallene (**5c**) were detected (Scheme V). It may be that the sterically hindered allene episulfide moiety of **6** could not make an empty site for $\eta^4(\pi)$-coordination.

The oxyallyl complex has recently been described as an η^3-oxodimethylenemethane or metallacyclobutanone structure;[6f–j] therefore the η^4-thioallyl complex should be interesting and important. The differences between these two structures may be correlated with the differences between ionic oxyallyl and radical thioallyl intermediates.

Supplementary Material Available: Detailed information of the X-ray crystal analysis of **2b** and **3** (30 pages). Ordering information is given on any current masthead page.
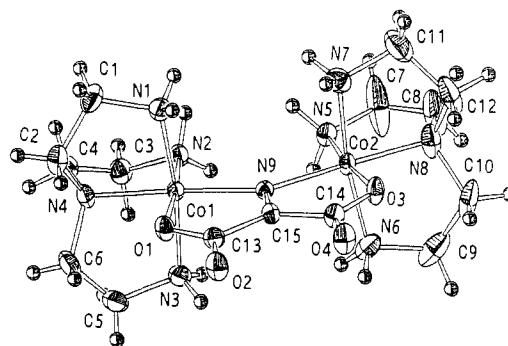

Figure 1. ORTEP representation of the structure of complex **1** at the 50% probability level. Selected bond lengths (Å) and interbond angles (deg): Co1–N1, 1.954 (6); Co1–N2, 1.938 (6); Co1–N3, 1.951 (6); Co1–N4, 1.953 (6); Co2–O3, 1.905 (5); Co2–N5, 1.949 (6); Co2–N6, 1.961 (7); Co2–N7, 1.957 (7); Co2–N8, 1.947 (6); Co1–N9, 1.991 (5); Co2–N9, 1.970 (5); N9–C15, 1.277 (9); Co1–O1, 1.917 (5); Co2–O3, 1.905 (5); Co1–N9–Co2, 142.9 (3); Co1–N9–C15, 108.7 (4); Co2–N9–C15, 108.3 (4); O1–Co1–N2, 174.6 (2); N1–Co1–N3, 172.0 (3); N4–Co1–N9, 172.7 (2); O1–Co1–N9, 84.3 (2); O3–Co2–N5, 174.2 (2); N6–Co2–N7, 171.1 (3); N8–Co2–N9, 173.8 (2); O3–Co2–N9, 85.5 (2).

Unprecedented Imido-Bridged Binuclear Cobalt(III) Complex: Synthesis and Molecular Structure of p-[Co2(μ-(μ2-N:η1-O,O')-imidomalonato)(tren)2](ClO4)3·H2O

Takahiko Kojima and Masanobu Hidai*

*Department of Synthetic Chemistry
Faculty of Engineering, The University of Tokyo
Hongo, Bunkyo-Ku, Tokyo 113, Japan*

Reiko Kuroda

*Department of Chemistry
College of Arts and Sciences, The University of Tokyo
Komaba, Meguro-Ku, Tokyo 153, Japan*

Shigenobu Yano

*Department of Chemistry, Faculty of Science
Nara Women's University, Nara-City, Nara 630, Japan*

Previously, we reported that, in the reaction of α-aminomalonate anion (AM^{2-}) with cobalt(III)–polyamine complexes,[1,2] C–N bond formation between the sp^3 α-carbon of AM^{2-} and one of the coordinated amino groups of the ligands, such as en^3 and 2,3,2-tet,[3] occurs, giving α-diamine complexes in moderate yield. This reaction has been assumed to take place via the formation of an iminomalonato intermediate.[1] We have now tried a similar reaction using tren^3 as the ligand, but no α-diamine complexes were

obtained. However, an unprecedented imidomalonato-bridged binuclear Co(III) complex was isolated in moderate yield. In this paper we describe the synthesis and characterization of the novel binuclear complex.

To a stirred suspension of [CoCl2(tren)]Cl·H2O[4] (4 mmol), NH4AMH (4 mmol), and charcoal (1 g) in methanol (250 mL), was added triethylamine (40 mmol) slowly. The temperature of the reaction mixture was kept in the range 50–60 °C for 5 h. The mixture was filtered to remove charcoal, evaporated to dryness, and resolved in ca. 2 L of water to adsorb on an SP-Sephadex C-25 cation-exchange resin column. The column was eluted by 0.2 M NaCl(aq), and a main pink fraction was collected. Crystals[5] suitable for X-ray crystallography were obtained by exchanging Cl⁻ with ClO4⁻ in water with the addition of LiClO4 followed by recrystallization.

A perspective view of a molecule of p-[Co2(μ-imido-malonato)(tren)2]$^{3+}$ (**1**)[6] is shown in Figure 1. No t-isomer was obtained. The two cobalt atoms are linked by the imido nitrogen atom and two carboxyl groups. The molecule has C_{2v} symmetry, and the geometry around each of the two cobalt centers is octahedral with four sites for tren ligands and two for the bridged imidomalonato ligand.[7] The distances of Co(1)–N(9) and Co-(2)–N(9) are 1.991 (5) and 1.970 (5) Å, respectively. The bonds are much longer than the reported values for Co(III)–N(imine) bonds.[8] An EHMO calculation[9] for complex **1** showed that the orbital interactions between the imido nitrogen and two Co atoms are weak σ and π types and the negotiated position of N(9) was suitable for binding to two Co centers. This caused the lengthening

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(3) Abbreviations: en = ethylenediamine; 2,3,2-tet = 3,7-diaza-1,9-diaminononane; 3,2,3-tet = 4,7-diaza-1,10-diaminodecane; tren = tris(2-aminoethyl)amine.

(4) Kimura, E.; Young, S.; Collman, J. P. *Inorg. Chem.* **1970**, *9*, 1183–1191.

(5) Anal. Calcd for C15H36N9O4Co2(ClO4)3·H2O: C, 21.43; H, 4.56; N, 14.99. Found: C, 21.45; H, 4.53; N, 14.50. Crystal data: monoclinic, $P2_1/n$, T = 23 °C, a = 12.603 (2) Å, b = 13.828 (2) Å, c = 17.889 (2) Å, β = 93.941 (8)°, Z = 4, V = 3110 (1) Å^3, D_{calcd} = 1.80 g cm^{-1}, D_{obsd} = 1.80 g cm^{-1}, unique data = 7481, observed data = 4713 (I > 3σ(I)), μ (Mo Kα) = 14.08 cm^{-1}, R = 0.069, R_w = 0.100. The disordering of perchlorate anion resulted in higher R and R_w values. A Rigaku AFC5R automated four-cycle diffractometer was used to collect intensity data. All the calculations were performed on a μ VAX-II by using the TEXSAN program system (Molecular Structure Corporation, Texas, 1987).

(6) A p-isomer possesses a substituent of highest priority at the position trans to an NH2 site; a t-isomer has the substituent at the position trans to tertiary N.

(7) ^{13}C NMR data in D2O (ppm, dioxane as a reference): 46.1, 47.0, 59.9, 62.7 (CH2 of tren), 168.6 (>C=N⁻), 183.6 (COO⁻).

(8) (a) Yamaguchi, M.; Yamagishi, T.; Hida, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1942–1944. (b) Harrowfield, J. M.; Sargeson, A. M.; Springborg, J.; Snow, M. R.; Taylor, D. *Inorg. Chem.* **1983**, *22*, 186–193.
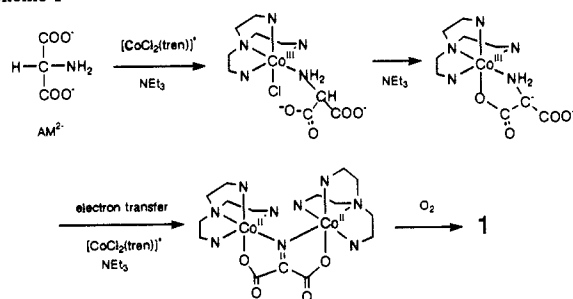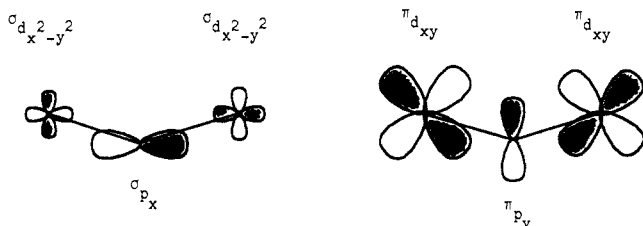
(9) The calculation was performed for a model complex, [Co2(μ-imido-malonato)(NH3)8]$^{3+}$. The parameters were taken from the reported values: (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397. (b) Hoffmann, R.; Lipscomb, W. L. *J. Chem. Phys.* **1962**, *36*, 2179.

Scheme I

of the two Co–N(imido) bonds and the widening of the Co(1)–N(9)–Co(2) angle (142.9 (3)°).

The polarogram[10] of **1** in H_2O showed two 1e⁻ reduction waves corresponding to two quasireversible redox couples,[11] [Co(III),-Co(III)] ↔ [Co(III),Co(II)] and [Co(III),Co(II)] ↔ [Co(II),-Co(II)] (E_{exp} = –0.05 and –0.28 V vs SCE, respectively), and an additional irreversible[11] 2e⁻ reduction wave due to the reduction of the imido group at –0.91 V.[12] Similar reduction waves were also observed at E_{exp} = –0.28, –0.46, and –1.07 V in a MeOH–DMF (1:1) solution. It is noteworthy that the Co(III)–Co(II) mixed valence state can be formed electrochemically in H_2O and in a MeOH–DMF (1:1) mixed solution.

The absorption spectrum of **1** in H_2O[13] showed a large red shift from the typical spectrum of the Co(III)–N_5O chromophore of p-isomers in the tren system[4] and was similar to that of t-isomers. The absorption spectra of Co(III)–α-imino acid complexes show a similar red shift by the deprotonation of the coordinated imino groups.[8a,14] The weakness of the Co–N(imido) bonds reduces the ligand field of two Co(III) ions in complex **1**.

In the case of en and 3,2,3-tet[3] used as polyamine ligands, α-diamine formation took place under N_2 via electron transfer accompanying the radical formation of AM^{2-}.[15] In contrast, as mentioned above, α-diamine formation was not observed when tren was used as an amine component. The structure of the tren moiety in complex **1** exhibits distortion toward the tertiary amino group, and this makes it difficult for the primary amino groups to attack the imine carbon. However, the isolation of the complex **1** having the imidomalonato provides strong evidence that the oxidation of AM^{2-} to the imidomalonato intermediate is performed through electron transfer to the two cobalt(III) ions and α-diamine formation should be performed with the aid of two metal centers. It is assumed that, in the tren system under air, an intermediate, $[Co(II)_2(\mu\text{-imidomalonato})(tren)_2]^+$, is oxidized by air to afford **1**. The proposed mechanism for the formation of **1** was represented in Scheme I.

The reaction temperature is important for the formation of complex **1**, since p-[Co(glycinato)(tren)]²⁺[4] was obtained instead of **1** when the reaction mixture was refluxed. The geometry of the glycinato complex is consistent with **1**.

In summary, a binuclear Co(III) complex **1** containing a novel μ_2-imido ligand has been prepared and characterized and it represents the existence of an imine intermediate and a binuclear pathway for α-diamine formation between AM^{2-} and Co(III)–polyamine complexes.

Supplementary Material Available: Listing of positional and thermal parameters for the title compound (4 pages); table of observed and calculated structure factors for the title compound (32 pages). Ordering information is given on any current masthead page.

Intercalation of Bis(ethylenedithio)tetrathiafulvalene (ET) into Iron Oxychloride: A Highly Conducting Low-Dimensional System

Joseph F. Bringley,[1a,b] Jean-Marc Fabre,[1c] and Bruce A. Averill*,[1a]

Department of Chemsitry
University of Virginia
Charlottesville, Virginia 22901
Laboratoire de Chimie Structurale Organique
U.S.T.L., 34060 Montpellier, France

Efforts to prepare new organic conducting materials have focused primarily on the preparation of new organic donors or modification of existing donors.[2] In our laboratory, we have been exploring an alternative approach to the synthesis of low-dimensional conductors that involves the use of layered materials as macroanionic electron acceptors and as matrices to enforce a particular structural arrangement upon an array of electron donor molecules. The synthetic method we have utilized is the intercalation[3] of planar electron donors such as aromatic hydrocarbons,[4] TTF,[5] TSF,[6] and related molecules[7] into the van der Waals gap

(10) A hanging-mercury-drop electrode was used as a working electrode. (a) In H_2O: I = 0.1 M KNO_3, 25 °C under Ar. (b) In MeOH–DMF (1:1): I = 0.1 M [(n-C_4H_9)₄N]ClO_4, 25 °C under Ar.

(11) The cyclic voltammogram with a hanging-mercury-drop electrode supports the two quasireversible 1e⁻ redox reactions and the irreversible 2e⁻ reduction.

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* Author to whom correspondence should be addressed.

(1) (a) University of Virginia. (b) Present address: IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY 10598. (c) Laboratoire de Chimie Structurale Organique, U.S.T.L., Montpellier, France.

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