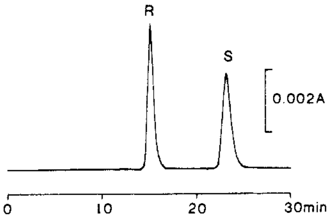

Figure 2. Chromatographic resolution of propranolol. Column 250 × 5 (i.d.) mm; eluent, sodium-acetate buffer pH 4.7, $I = 0.01$, containing 0.5% 2-propanol; (*RS*)-propranolol was dissolved in the eluent; 20 μL of the solution (6 × 10^{-5} mol/L) was injected; flow rate 0.3 mL/min, temperature 22 °C; UV detection at 254 nm. The elution order was established by injecting the pure enantiomers.

Hermansson has successfully used the plasma protein α_1-acid glycoprotein (AGP or orosomucoid) as a chiral stationary phase (CSP) for liquid chromatographic separations of enantiomers.[9] It has been suggested that the carbohydrate domain of AGP, about 45% of the molecular weight, is involved in the chiral recognition.[10] Proteins without carbohydrates, e.g., bovine serum albumin,[11,12] and carbohydrates without proteins, e.g., cellulose,[13,14] have also been utilized as CSPs.

In this study we report briefly the preparation and use of a CSP based on one cellulase, CBH I. Salts and pigments were removed from the crude culture filtrate of *T. reesei QM 9414* by gel chromatography. Ion-exchange chromatography was used for all remaining purification steps.[15] The homogeneity was tested by SDS–PAGE and IEF–PAGE.[15] The cellulase (CBH I) was covalently bonded to aldehyde silica (particle size 10 μm) according to the following method. The aldehyde silica, obtained by oxidation of diol silica by periodic acid, and sodium cyanoborohydride were added to a phosphate buffer solution (pH 7) of CBH I. The Schiff's base obtained was reduced by sodium cyanoborohydride to get a stable covalent bond between the cellulase and the silica derivative. The CSP was washed on a sintered-glass filter with the buffer solution. Finally, the material was packed into a steel column (250 × 5 mm i.d.) by using a descending slurry-packing technique.

Examples of direct resolution of racemic drugs (Figure 1) are given in Table I. Alprenolol, metoprolol, propanolol (Figure 2) (β-adrenergic blockers), prilocaine (local anesthetic), and warfarin (anticoagulant) were all well resolved with high stereoselectivity on this cellulase-based CSP using aqueous mobile phases. A surprisingly high stereoselectivity was obtained for alprenolol (α = 8.3).

The cellulase–silica material seems to be a promising contribution to the pool of CSPs. The fact that the cellulases are available in huge quantities indicates their potential as chiral selectors in preparative as well as analytical applications.

Acknowledgment. This work was supported by the National Swedish Board for Technical Development and the Swedish Natural Science Research Council.

Registry No. Alprenolol, 13655-52-2; Metopralol, 37350-58-6; prilocaine, 721-50-6; propanolol, 525-66-6; warfarin, 81-81-2.

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(Thioallyl)iron Tricarbonyl Complex by the Reaction of Allene Episulfides with Diiron Nonacarbonyl

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Received January 22, 1990

Tautomerism of allene episulfide and cyclopropanethione via a thioallyl intermediate[1,2] is of great interest since these entities are the sulfur analogues of the well-studied allene oxide–cyclopropanone–oxyallyl[3] and methylenecyclopropane–trimethylide systems[4] (Scheme I). According to the kinetic[2f–i] and MCSCF calculation studies,[2e,g] thioallyl is a biradical with partial ionic character similar to trimethylenemethane[3c] rather than oxyallyl.[4c–e] Recently, we proposed the thioallyl cation to account for the acid-catalyzed isomerization of allene episulfide.[5] Meanwhile thioallyl biradical would be expected to be easily complexed with metals such as (trimethylenemethane)iron tricarbonyl.[6a,b] We now report the formation of the new type of (η^4-thioallyl)tricarbonyliron complex obtained from the reaction of allene episulfide with diiron nonacarbonyl.

Tetramethylallene episulfide (**1a**)[2a] was treated with 1.2 equiv of diiron nonacarbonyl in benzene at 60 °C for 10 min. After the solvent was removed at reduced pressure, the residue was separated by preparative HPLC, and subsequent recrystallization from hexane gave rise to two iron carbonyl derivatives, **2a** ($Me_4C_3SFe(CO)_3$, 16%) and **3** ($Me_4C_3Fe_2(CO)_6$, 11.5%), and 1-isopropenyl-2-methyl-1-propenyl) disulfide **4** (6.5%) (see Scheme II). In contrast, a reaction with aryl- and *tert*-butyl substituted allene episulfide **1b** provided single iron carbonyl complex **2b** (${}^tBuPh_2C_3HSFe(CO)_3$, 29%) along with diaryl-*tert*-butylallene **5b** (25%) (Scheme III). The molecular formulas and group assignments shown in parentheses are based on mass, ^1H and ^{13}C NMR, and IR spectral analysis.[7] Compounds **2a** and **2b** were

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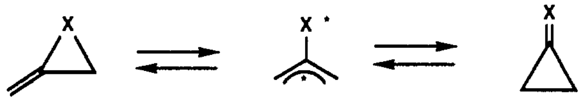
(6) For trimethylenemethane complex: (a) Churchill, M. R.; Gold, K. *J. Chem. Soc., Chem. Commun.* **1968**, 693. (b) Ehrlich, K.; Emerson, G. F. *J. Am. Chem. Soc.* **1972**, *94*, 2464. (c) Trost, B. M.; Chan, D. M. T. *Ibid.* **1983**, *105*, 2326. (d) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. (e) Jones, M. D.; Kemmitt, R. D. W.; Platt, A. W. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1411. For oxyallyl complex: (f) Fawcett, J.; Henderson, W.; Jones, M. D.; Mekkitt, R. D. W.; Russell, D. R.; Lam, B.; Kang, S. K.; Albright, T. A. *Organometallics* **1989**, *8*, 1991. (g) Jones, M. D.; Kemmitt, R. D. W.; Fawcett, J.; Russell, D. R. *J. Chem. Soc., Chem. Commun.* **1986**, 427. (h) Imran, A.; Kemmitt, R. D. W.; Markwick, A. J. W.; McKenna, P.; Russell, D. R.; Sherry, L. J. S. *J. Chem. Soc., Dalton Trans.* **1985**, 549. (i) Kemmitt, R. D. W.; McKenna, P.; Russell, D. R.; Sherry, L. J. S. *Ibid.* **1985**, 259. (j) Holmgren, J. S.; Shapley, J. R.; Wilson, S. R.; Pennington, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 508.

0002-7863/90/1512-4574$02.50/0

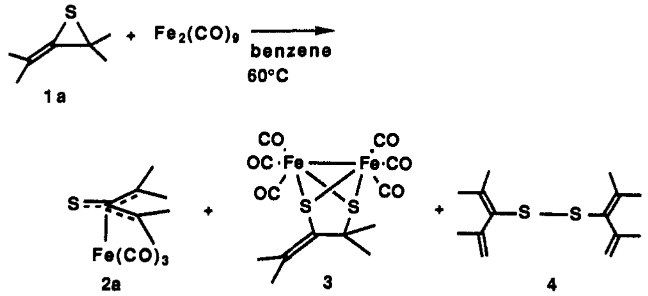
Scheme I



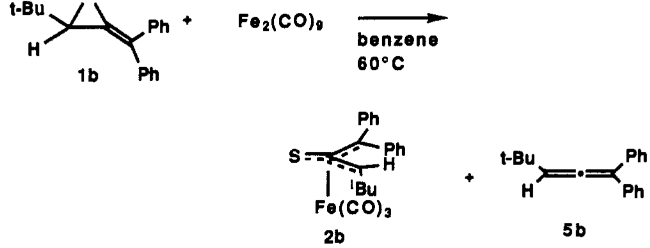
• = radical or ion

X = CH_2, O, S

Scheme II



Scheme III



stable yellow and orange crystalline materials with mp 59–60 °C and 111.5–112.5 °C, respectively. The common fragments of $C_3SFe(CO)_3$ in **2a** and **2b** exhibit two distinct CO absorptions from 1950 to 2100 cm^{-1} in the IR spectra and two or three sets of olefinic signals in the ^{13}C NMR spectra. At room temperature, the carbonyl ligands at iron are fluxional in **2a** with one broad carbonyl signal in ^{13}C NMR but not in **2b** as indicated by the three distinct carbonyl signals in the ^{13}C NMR spectra. These spectroscopic data demand the (η^4-thioallyl)iron tricarbonyl structure for **2a** and **2b** shown in the schemes. An X-ray structure determination of **2b**[8] provided confirmation. The ORTEP drawing of **2b** is shown in Figure 1 together with the more important bond distances and angles. The iron atom is located directly beneath the central atom (C1) of the thioallyl residue and is π-bonded to three carbon atoms and one sulfur atom of this ligand. This unit can be regarded as a significant trimethylenemethane moiety. The relevant bond distances C1–S, C1–C2, and C1–C3 are 1.757, 1.414, and 1.40 Å, respectively. These may be between C–S or C–C single and double bonds. With the inspection of Figure 1, the thioallyl ligand and iron tricarbonyl moiety adopt a mutually staggered conformation. The structure of compound **3**, deep red crystalline, was assigned by comparison with the published data of the analogous complex $[Me_4C_3SOFe_2(CO)_6]$,[9a] and its butterfly structure was finally confirmed by X-ray analysis.[9b]

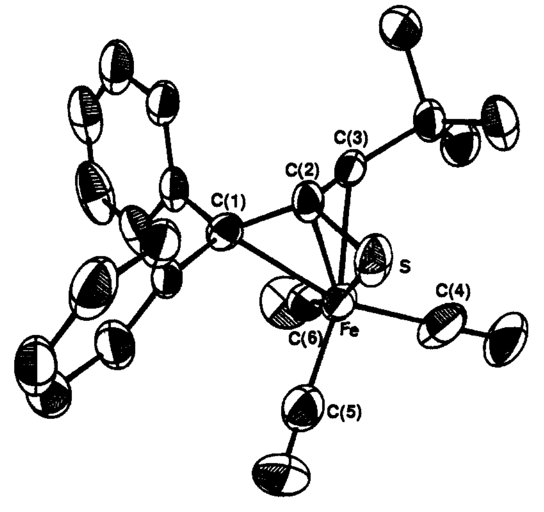
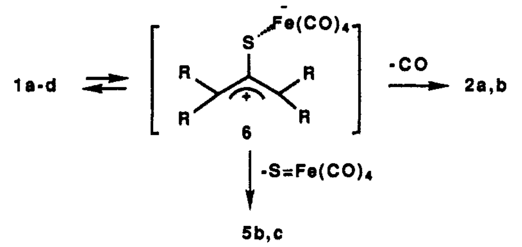
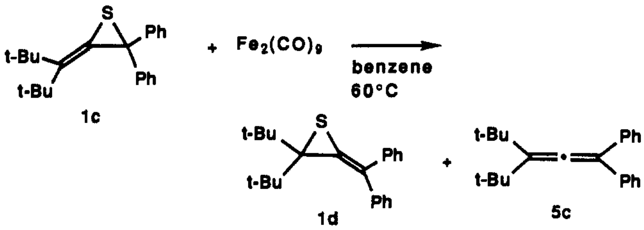


Figure 1. ORTEP drawing of **2b**. Selected bond lengths (angstroms) (Å) and angles (degrees): S–C(1), 1.757 (8); C(1)–C(2), 1.41 (1); C(1)–C(3), 1.40 (1); Fe–S, 2.308; Fe–C(1), 1.938; Fe–C(2), 2.262; Fe–C(3), 2.180; Fe–C(4), 1.80 (1); Fe–C(5), 1.84; Fe–C(6), 1.76 (1). S–C(1)–C(2), 115.2; S–C(1)–C(3), 116.9; C(2)–C(1)–C(3), 119.2; S–C(1)–Fe, 77.2; C(2)–C(1)–Fe, 83.4; C(3)–C(1)–Fe, 79.7.

Scheme IV



Scheme V



The most reasonable first step of the process by which the complexes **2a** and **2b** are formed, C–S bond cleavage of allene episulfide by $Fe(CO)_4$, is shown in Scheme IV, a reaction that finds precedents.[10] Next, the resulting thioallyl cation complex

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(7) **2a**: yellow crystals; mp 59–60 °C; ^1H NMR (500 MHz, C_6D_6) δ 1.49 (s, 6 H), 1.89 (s, 6 H); ^{13}C NMR (125 MHz, C_6D_6) δ 27.5 (q), 30.4 (q), 105.1 (s), 117.9 (s), 210.1 (br s); IR (*n*-hexane) ν 2080 (s), 2000 (s), 1960 (w) (CO) cm^{-1}; MS, *m/z* 268 (M^+, 9), 240 (63), 212 (42.5), 184 (70), 81 (100); HRMS calcd for $C_{10}H_{12}FeO_3S$ 267.9855, found 267.9828. **2b**: orange crystals, mp 111.5–112.5 °C; ^1H NMR (C_6D_6) δ 1.16 (s, 9 H), 4.33 (s, 1 H), 6.73–7.53 (m, 10 H); ^{13}C NMR (125 MHz, C_6D_6) δ 32.26 (q), 36.22 (s), 106.34 (d), 118.56 (s), 122.60 (s), 126.88 (d), 127.15 (d), 127.24 (d), 128.32 (d), 130.57 (d), 131.97 (d), 142.68 (s), 144.30 (s), 209.06 (s), 209.48 (s), 210.12 (s); IR (*n*-hexane) ν 2080 (s), 2020 (s) (CO) cm^{-1}; MS, *m/z* 420 (M^+, 4), 364 (56), 336 (100), 301 (83), 244 (27), 192 (41.6). Anal. Calcd for $C_{22}H_{20}FeO_3S$: C, 62.86; H, 4.79. Found: C, 62.90; H, 4.74. **3**: orange crystals; mp 106.5–107 °C; ^1H NMR ($CDCl_3$) δ 1.59 (s, 6 H), 1.73 (s, 3 H), 2.11 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.98 (q), 26.97 (q), 30.50 (q), 56.16 (s), 136.23 (s), 137.36 (s), 208.81 (br s); IR (*n*-hexane) ν 2060 (s), 2030 (s), 2000 (sh), 1995 (s), 1985 (sh), 1950 (w) (CO) cm^{-1}; MS, *m/z* 440 (M^+, 21), 412 (26.5), 384 (41), 356 (26.5), 328 (14.3), 300 (69.6), 272 (100). Anal. Calcd for $C_{13}H_{12}Fe_2O_6S_2$: C, 35.47; H, 2.74. Found: C, 35.65; H, 2.71.

(8) Crystal data for **2b**: $C_{22}H_{20}FeO_3S$, $M = 420.31$, monoclinic with $a = 11.437$ (4) Å, $b = 7.003$ (3) Å, $c = 25.235$ (9) Å, $\beta = 91.37$ (3)°, $V = 2020.7$ Å^3, space group $P21/c$, $Z = 4$, $\mu(\mathrm{Mo}\ K\alpha) = 8.6$ cm^{-1}, $\rho_{\mathrm{calcd}} = 1.38$ g/cm^3. The 7260 independent reflections $[|F_o| > 3\sigma|R_o|, \theta < 50°]$ were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and an ω–2θ scan. The structure was solved by direct methods, and all nonhydrogen atoms were refined anisotropically by full-matrix least squares to $R = 0.091$ and $R_w = 0.107$.

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7

8

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.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas (No. 01648001) from the Ministry of Education, Science and Culture, Japan.

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.

Unprecedented Imido-Bridged Binuclear Cobalt(III) Complex: Synthesis and Molecular Structure of p-$[Co_2(\mu\text{-}(\mu_2\text{-}N{:}\eta^1\text{-}O,O')\text{-imidomalonato})(tren)_2](ClO_4)_3{\cdot}H_2O$

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Received February 5, 1990

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.

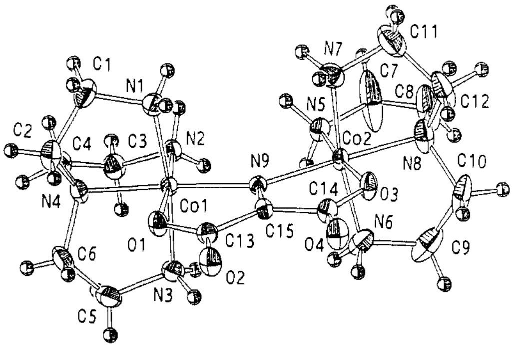

Figure 1. ORTEP representation of the structure of complex **1** at the 50% probability level. Selected bond lengths (Å) and interbond angles (deg): Co1–N1, 1.954 (6); Co1–N2, 1.938 (6); Co1–N3, 1.951 (6); Co1–N4, 1.953 (6); Co2–O3, 1.905 (5); Co2–N5, 1.949 (6); Co2–N6, 1.961 (7); Co2–N7, 1.957 (7); 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).

To a stirred suspension of $[CoCl_2(tren)]Cl{\cdot}H_2O$[4] (4 mmol), NH_4AMH (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 ClO_4^- in water with the addition of $LiClO_4$ followed by recrystallization.

A perspective view of a molecule of p-$[Co_2(\mu\text{-imidomalonato})(tren)_2]^{3+}$ (**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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[1] Yashiro, M.; Shimada, A.; Usui, T.; Yano, S.; Kobayashi, K.; Sakurai, T.; Yoshikawa, S. *J. Am. Chem. Soc.* **1985**, *107*, 4351–4353.

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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 $C_{15}H_{36}N_9O_4Co_2(ClO_4)_3{\cdot}H_2O$: 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, $\beta = 93.941$ (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 ($I > 3\sigma(I)$), 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 NH_2 site; a t-isomer has the substituent at the position trans to tertiary N.

[7] ^{13}C NMR data in D_2O (ppm, dioxane as a reference): 46.1, 47.0, 59.9, 62.7 (CH_2 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, $[Co_2(\mu\text{-imidomalonato})(NH_3)_8]^{3+}$. 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.