

Figure 1. Arrhenius plot of the rate data on **2**. The solid squares represent data from line shape analysis, and the open squares are taken from the magnetization transfer experiment.

On the basis of our calculations of the inversion barrier in the saturated ADPO system³ **4**, we would expect that the barrier in **3** would increase when the C=C bond is saturated. However, changing the Si to Ge^{1a} should approximately cancel the increase due to saturation. We therefore chose a saturated ligand system on a germanium center **2** which also provides steric hindrance to bimolecular processes and provides a convenient NMR handle for barrier determination.

Compound **2** was synthesized by the reaction of the amine-ol **1** with GeCl₄ in the presence of triethylamine in CH₂Cl₂. Compound **2** is a stable crystalline solid melting 121–124 °C. Consistent ¹H, ¹³C, and ¹⁵N NMR spectra and elemental analysis were obtained for **2**.¹⁰

Over the temperature range from 80 to 150 °C, the ¹H NMR spectrum of **2** was examined in toluene-*d*₈. Between 120 and 150 °C there was sufficient change in the line shape to allow determination of the inversion rate by standard analysis of the line shapes for the diastereotopic protons H_a and H_b. In the range from 90 to 130 °C the inversion rate was determined from a magnetization transfer experiment on the H_a and H_b protons. In the magnetization transfer experiment, selective inversion of the H_b doublet leads to a characteristic decrease in the intensity for the H_a resonance in the ¹H NMR spectrum and indicates that inversion is occurring at a rate comparable to spin-lattice relaxation.

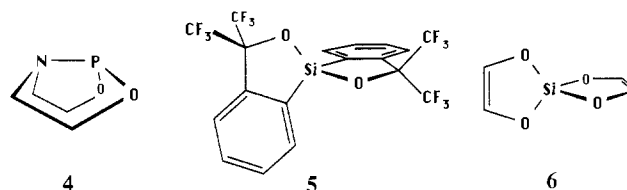
The rate data from the ¹H NMR experiments are plotted in Arrhenius form in Figure 1. From a nonlinear least-squares fit to the Eyring equation¹¹ we obtain $\Delta H^\ddagger = 22.2 \pm 2.5$ kcal/mol

(10) A sample of **2** recrystallized from toluene/acetonitrile gave mp 121–124 °C: Anal. (C₃₆H₄₆N₂O₂Ge) C, H, N, Ge. ¹H NMR (CD₂Cl₂) δ 1.40–1.77 (m, adamantyl, 24 H), 2.30 (dm, *J* = 11.7 Hz, adamantyl, 4 H), 2.78 (d, ²*J*_{HH} = 9.5 Hz, H_a, 2 H), 2.84 (d, ²*J*_{HH} = 9.5 Hz, H_b, 2 H), 4.05 (d, ²*J*_{HH} = 14.0 Hz, CH₂-phenyl, 2 H), 4.09 (d, ²*J*_{HH} = 14.0 Hz, CH₂-phenyl, 2 H), 7.20–7.40 (m, aromatic, 10 H); ¹H NMR (toluene-*d*₈) δ 1.40–1.90 (m, adamantyl, 24 H), 2.62 (dm, *J* = 12.0 Hz, adamantyl, 4 H), 2.63 (d, ²*J*_{HH} = 9.3 Hz, H_a, 2 H), 2.85 (d, ²*J*_{HH} = 9.3 Hz, H_b, 2 H), 3.98 (d, ²*J*_{HH} = 14.1 Hz, CH₂-phenyl, 2 H), 4.02 (d, ²*J*_{HH} = 14.1 Hz, CH₂-phenyl), 7.09 (tm, *p*-phenyl, 2 H), 7.20 (dd, *m*-phenyl, 4 H), 7.35 (dm, *o*-phenyl, 4 H). At 100 °C in toluene-*d*₈ the following resonances are noticeably shifted from the ambient temperature spectra listed above: δ 2.57 (dm, *J* = 12.7 Hz, adamantyl, 4 H), 2.71 (d, ²*J*_{HH} = 9.3 Hz, H_a, 2 H), 2.95 (d, ²*J*_{HH} = 9.3 Hz, H_b, 2 H), 3.98 (d, ²*J*_{HH} = 14.0 Hz, CH₂-phenyl, 2 H), 4.02 (d, ²*J*_{HH} = 14.0 Hz, CH₂-phenyl, 2 H); ¹³C NMR (toluene-*d*₈) δ 27.46 (CH), 28.13 (CH), 33.50 (CH₂), 33.61 (CH₂), 34.89 (CH₂), 35.01 (CH₂), 38.06 (CH), 38.48 (CH₂), 38.54 (CH), 53.21 (CH₂-phenyl), 57.18 (NCCO), 79.02 (CO), 127.29 (*p*-phenyl), 128.41 (*m*-phenyl), 128.58 (*o*-phenyl), 140.91 (*ipso*-phenyl); ¹⁵N NMR (toluene-*d*₈) δ -283.0 (reference NH₄NO₃).

(11) Atkins, P. W. *Physical Chemistry*, 2nd. ed.; W. H. Freeman & Company: San Francisco, 1982; pp 978–987.

and $\Delta S^\ddagger = 0.65 \pm 6.5$ eu. The value for ΔH^\ddagger is significantly less than would be expected for a process involving bond-breaking and is in excellent accord with expectations based on our calculations (vide supra). The unimolecularity is supported by the near zero ΔS^\ddagger and the concentration independence of the inversion rate. Reduction of the concentration of **2** by half yields the same inversion rates. Addition of 50 mol % of pyridine resulted in a very rapid inversion rate ($\sim 10^3$ times faster).¹² In more nucleophilic solvents, the inversion rate was also accelerated, $\Delta H^\ddagger = 17.96 \pm 1.31$ kcal/mol and $\Delta S^\ddagger = -9.4 \pm 3.6$ eu in *o*-dichlorobenzene-*(d)*₄. Thus, when nucleophiles are available a very rapid nucleophile assisted inversion can contribute to the observed rate.

These results provide confirmation of the operation of an unassisted edge inversion process at main group IV centers in the absence of nucleophiles. Our results are in accord with the recent work by Martin^{13,14} on **5** and are significantly lower than low level calculations¹⁵ on the barrier for **6**.



Clearly with careful design of the ligand system unassisted edge inversion of a main group IV system is possible.

Acknowledgment is made to F. Davidson for preliminary rate measurements on the nucleophile assisted inversions.

(12) (a) Dixon, D. A.; Arduengo, A. J., III *Int. J. Quantum Chem. Symp.* **1988**, in press. (b) Arduengo, A. J., III; Dixon, D. A.; Kline, M.; Roe, D. C., to be submitted for publication.

(13) A lower limit of 28 kcal/mol has been estimated for this inversion process and represents an upward revision of the number reported in ref 14: Martin, J. C.; Henderson, C., private communication.

(14) Martin, J. C.; Stevenson, W. H., III; Lee, D. Y. In *Organosilicon and Bioorganosilicon Chemistry: Structure, Bonding, Reactivity and Synthetic Application*; Sakurai, H., Ed.; Ellis Horwood: Chichester, U.K., 1985; Chapter 13, p 141.

(15) Wurthwein, E.-U.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 553.

An Allene Adduct of Ditungsten Hexa-*tert*-butoxide: Prediction of a Stabilized μ - η^3 -CH₂CCH₂ Moiety

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Reactive hydrocarbyl fragments are often stabilized by coordination to transition metals,¹ though rarely have these species been predicted. A notable exception was the prediction by Longuet-Higgins and Orgel² of cyclobutadiene-metal complexes. We wish here to report the preparation of a 1:1 adduct between allene and W₂(O-*t*-Bu)₆, and, on the basis of the observed spectroscopic data and theoretical considerations, we propose the existence of a central W₂(μ - η^3 -C₃H₄) moiety in which the allenic π orbitals resemble the predicted transition state for allene isomerization.³

Hexane solutions of W₂(O-*t*-Bu)₆ and allene (1 atm.) react at 0 °C to give a green solution from which dark green crystals, W₂(O-*t*-Bu)₆(C₃H₄) have been obtained analytically pure⁴ by

(1) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

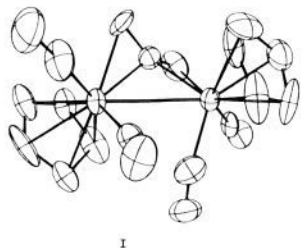
(2) Longuet-Higgins, H. C.; Orgel, L. E. *J. Chem. Soc.* **1956**, 1969.

(3) Voltzanos, P.; Elbert, S. T.; Ruedenberg, K. *J. Am. Chem. Soc.* **1986**, *108*, 3147.

cooling the solution to $-20\text{ }^{\circ}\text{C}$. The compound $\text{W}_2(\text{O}-t\text{-Bu})_6(\text{C}_3\text{H}_4)$ decomposes in solution at room temperature to give amongst other products $(t\text{-BuO})_3\text{W}\equiv\text{CMe}^{5,6}$ and $(t\text{-BuO})_3\text{W}\equiv\text{CH}^7$. Presumably these arise from an allene to propyne isomerization at the metal center. Attempts to prepare related 1:1 allene adducts involving other $\text{W}_2(\text{OR})_6$ compounds where $\text{R} = i\text{-Pr}$, $\text{CH}_2\text{-}t\text{-Bu}$, and cyclohexyl lead to the rapid uptake of 2 equiv of allene, even when only 1 equiv is added, and further coupling and hydrogen migrations occur.⁸ Thus at this time $\text{W}_2(\text{O}-t\text{-Bu})_6(\text{C}_3\text{H}_4)$ is the only member of its class.

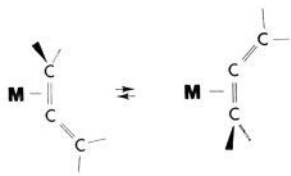
The ^1H NMR spectra of $\text{W}_2(\text{O}-t\text{-Bu})_6(\text{C}_3\text{H}_4)$ in toluene- d_8 and toluene- d_8 /freon-12 in the temperature range 0 to $-130\text{ }^{\circ}\text{C}$ are temperature invariant and reveal two types of O- t -Bu ligands in the ratio 2:1 and one type of allenic proton at 7.03 ppm⁹ with coupling to ^{183}W , $I = 1/2$, 14.5% natural abundance, $J_{\text{W-H}} = 6.2$ Hz. The satellite intensity requires a coupling to two equivalent tungsten atoms. The $^{13}\text{C}\{^1\text{H}\}$ spectrum is also temperature invariant and shows two types of O- t -Bu groups in the integral ratio 2:1 and two allenic carbon signals, δ 249.7 and 89.1, assignable to the quaternary and methylenic carbon atoms, respectively.⁹ Both signals show coupling to two equivalent tungsten nuclei as evidenced by the intensity of the tungsten satellites. No exchange between free and coordinated allene is observed by NMR spectroscopy.

Previously it has been shown¹⁰ that allene binds to $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{M}\equiv\text{M})$ to give a 1:1 adduct in which a V-shaped C_3 fragment spans the Mo-Mo vector. Each $\text{C}=\text{CH}_2$ moiety interacts independently with each Mo atom as schematically shown in I below. This type of bonding generates a C_2 molecular axis of symmetry for the $\text{M}_2(\mu\text{-C}_3\text{H}_4)$ moiety and two types of allenic protons. This static structure was apparently maintained in solution for $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_3\text{H}_4)$.¹⁰



I

It is known in mononuclear metal chemistry that allene can "hop" from one π bond to the other as depicted by II and III below.



II

III

This causes an averaging of the allenic substituents. The transition

(4) Anal. Calcd (found) for $\text{C}_{29}\text{H}_{58}\text{O}_6\text{W}_2$: C, 38.30 (38.24); H, 6.90 (6.74). Anal. Calcd (found) for $\text{W}_2(\text{O}-t\text{-Bu}-d_9)_6(\text{C}_3\text{H}_4)$, $\text{C}_{27}\text{H}_4\text{D}_{54}\text{O}_6\text{W}_2$: C, 36.02 (35.77); H + D (as H), 6.49 (6.69). All crystals examined thus far have failed to yield good diffraction data, apparently because of twinning.

(5) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291; Schrock, R. R.; Listemann, M. L. *Organometallics* **1985**, *4*, 74.

(6) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.

(7) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

(8) Chisholm, M. H.; Hampden-Smith, M. J., unpublished results.

(9) NMR data for $\text{W}_2(\text{O}-t\text{-Bu})_6(\text{C}_3\text{H}_4)$. ^1H NMR (0 $^{\circ}\text{C}$, toluene- d_8): δ 7.03 (s, 4 H, $J_{\text{H-W}} = 6.2$ Hz, 29%, $\text{CH}_2=\text{C}=\text{CH}_2$), 1.75 (s, 18 H, O- t -Bu), 1.28 (s, 36 H, O- t -Bu). ^{13}C NMR (0 $^{\circ}\text{C}$, toluene- d_8): δ 249.7 ($J_{\text{C-W}} = 31$ Hz, 24%, $\text{CH}_2=\text{C}=\text{CH}_2$), 89.1 ($J_{\text{C-W}} = 33$ Hz, 22%, $J_{\text{C-H}} = 156$ Hz, $\text{CH}_2=\text{C}=\text{CH}_2$), 82.5 ($\text{OC}(\text{CH}_3)_3$), 78.0 ($\text{OC}(\text{CH}_3)_3$), 33.5 ($\text{OC}(\text{CH}_3)_3$), 31.5 ($\text{OC}(\text{CH}_3)_3$).

(10) Chisholm, M. H.; Rankell, L. A.; Bailey, W. I., Jr.; Cotton, F. A.; Murillo, C. A. *J. Am. Chem. Soc.* **1977**, *99*, 1261; **1978**, *100*, 802.

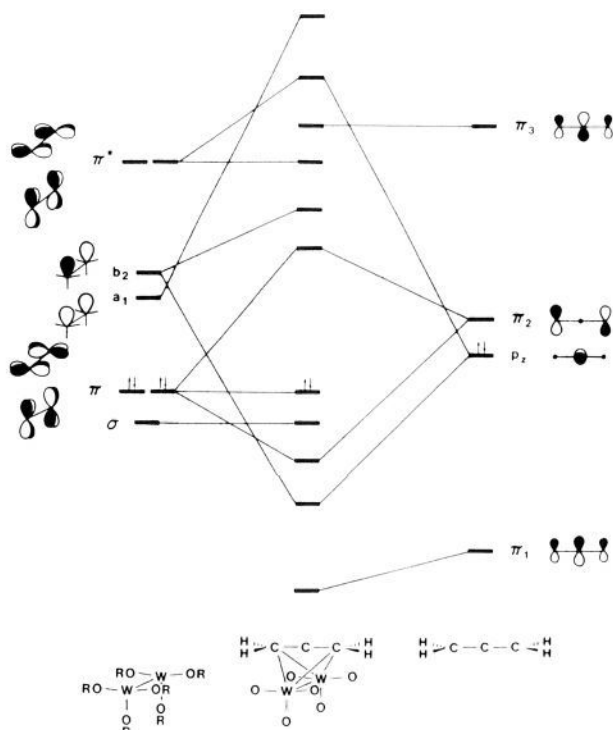
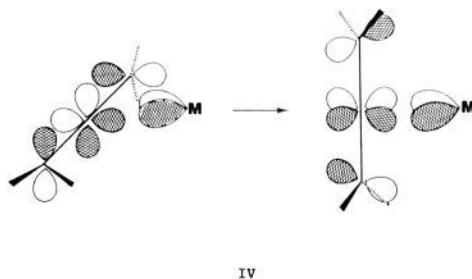


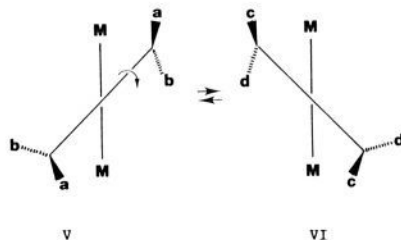
Figure 1. A qualitative orbital interaction diagram for a planar $\text{CH}_2\text{-C-CH}_2$ moiety and a $\text{W}_2(\text{OR})_6$ fragment. The relative orbital energies are considered reasonable estimates on the basis of calculations modeling $\text{W}_2(\text{OR})_6(\mu\text{-C}_2\text{H}_2)$ compounds.

state for this hopping does not require allene dissociation and can maintain the orthogonality of the $\text{C}=\text{C}$ bonds as shown in IV.¹¹



IV

Initially we considered that the allene might pivot about the C_2 axis of the $\text{W}_2(\mu\text{-C}_3)$ vector such that the NMR observations were a time average of structure V and VI. This type of motion requires both "rock and roll" in order to average all four allenic protons.¹²



V

VI

However, a μ -perpendicular allene to $\text{W}_2(\text{O}-t\text{-Bu})_6$ interaction can be shown to be nonbonding on the basis of symmetry argu-

(11) Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* **1967**, *89*, 2231. Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *In Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 363-364.

(12) A "rock" is defined as a ca. 45° twist of the allene about the pseudo- C_2 axis bisecting the M-M bond and a "roll" as a rotation by 90° about the allenic C-C axis. As shown in the interconversion of V and VI it requires two "rolls" in a consecutive clockwise or anticlockwise manner to make all four H atoms equivalent. Each "roll" is accompanied by a "rock".

ments. This caused us to examine alternate structures and in particular the interaction between a planar $\text{CH}_2\text{-C-CH}_2$ moiety and a $\text{W}_2(\text{O-}t\text{-Bu})_6$ group.

The interaction diagram shown in Figure 1 emphasizes the close analogy between the μ -perpendicular alkyne^{13,14} and the μ -perpendicular planar $\text{CH}_2\text{-C-CH}_2$ moiety. From Figure 1 we see that the μ - η^3 -allene behaves as a four-electron donor and a two-electron π -acceptor. On the basis of orbital overlap we would expect the C-C-C moiety to bend to maximize the W_2 to allene back-bonding. Note, too, that the allene orbitals that are receiving electron density from the W_2 moiety are formally allene non-bonding and thus will be close in energy to the tungsten-based orbitals leading to an overall strong six-electron bonding interaction. Only the allene π^* orbital is not involved. The predicted bend of this C-C-C fragment is opposite to that seen in $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{C}_3\text{H}_4)$ ¹⁰ and resembles the predicted transition state for allene isomerization.³ The latter has recently been predicted to have a C-C-C angle of 133° and an energy of activation of 42 kcal mol^{-1} .

The proposed structure of $\text{W}_2(\text{O-}t\text{-Bu})_6(\mu\text{-C}_3\text{H}_4)$ thus may closely resemble that of the μ -alkyne and CO adducts of formula $\text{M}_2(\text{OR})_6(\mu\text{-X})$ where $\text{X} = \text{CO}$ ¹⁵ or $\text{C}_2\text{R}_2'$.^{16,17}

(13) Hoffmann, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858.

(14) Chisholm, M. H.; Conroy, B. K.; Clark, D. L.; Huffman, J. C. *Polyhedron*, in press.

(15) The bonding in $\text{M}_2(\text{OR})_6(\mu\text{-CO})$ compounds is discussed in detail: Blower, P. J.; Chisholm, M. H.; Clark, D. L.; Eichhorn, B. W. *Organometallics* **1986**, *5*, 2125.

(16) For a general review of the chemistry of $\text{W}_2(\text{OR})_6(\mu\text{-C}_2\text{R}_2')$ compounds, see: Chisholm, M. H.; Conroy, B. K.; Eichhorn, B. W.; Foltz, K.; Hoffmann, D. M.; Huffman, J. C.; Marchant, N. S. *Polyhedron* **1987**, *6*, 783.

(17) We thank the National Science Foundation for support. R.H.C. is a Chester Davis Fellow, 1988.

An Unusual Dinuclear Cobalt Dioxxygen Complex with a Tetradentate Thioether-Imidazole-Containing Ligand. Structure of $[\text{Co}_2(\text{bidhx})_2(\text{O}_2)(\text{OH})](\text{NO}_3)_3$

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Many dinuclear, dioxxygen bridged cobalt(III) complexes are known.¹ Most of these dimers have the general formula $[\text{N}_4\text{Co}(\text{O}_2)(\text{OH})\text{CoN}_4]^{++}$, where N_4 corresponds to four nitrogen donor atoms, either bidentate (ethylenediamine²) or tetradentate (tris(2-aminoethyl)amine³). These compounds are of increasing interest from the point of view of oxygen activation and selective or specific oxidation reactions for organic molecules.⁴ The activity of dioxxygen complexes is strongly determined by the nature of the N_4 coligands. Especially cobalt complexes with 1,6-bis(2-hydroxyphenyl)-2,5-diaza-1,5-hexadiene (SALEN) or polyamines and related ligands have been employed successfully as catalysts.⁴⁻⁶

Cobalt(III) shows a particular affinity for nitrogen donor atoms.⁷ It is therefore to be expected that changing the N_4 -donor set of the coligand to N_2S_2 will change the possible oxygen-binding and catalytic properties. In a first attempt the ligand 1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane (bidhx), containing two

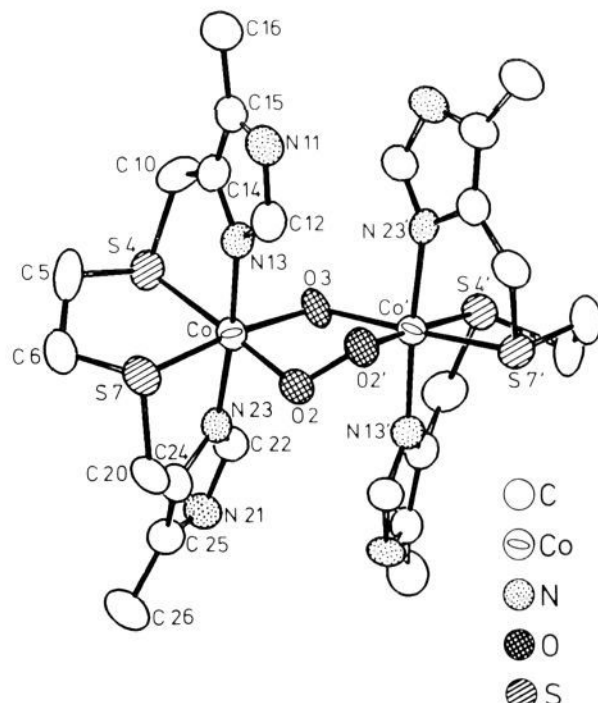


Figure 1. ORTEP projection of the dimeric cation $[\text{Co}_2(\text{bidhx})_2(\text{O}_2)(\text{OH})]^{3+}$, with thermal ellipsoids of 50% probability. The hydrogen atoms and the nitrate anions are omitted for clarity. The primed atoms are at the positions $1-x, y, 0.5-z$.

imidazole N atoms and two thioether S atoms, was used in a synthetic effort to prepare cobalt(II) compounds. Much to our surprise a dinuclear cobalt complex with bridging dioxxygen formed spontaneously, of which the synthesis and preliminary structure are described below.

The synthesis of the ligand bidhx and other thioether-imidazole-containing ligands has been described earlier.⁸ Addition of the tetradentate ligand bidhx (1 mmol) to cobalt nitrate (1 mmol) in aqueous ethanol (ca. 30 mL) gave a dark red solution, which, upon exposure to the air, yielded dark green crystals suitable for X-ray diffraction.⁹

The stoichiometry of the compound is $\text{Co}_2(\text{bidhx})_2(\text{H}_x\text{O})(\text{O}_2)(\text{NO}_3)_3$ with $x = 0, 1, \text{ or } 2$; the number of H-atoms cannot be obtained from the X-ray analysis. From the net electric charge it may be concluded that the cobalt ion may be either divalent or trivalent resulting in $\{\text{Co}(\text{II})\}_2$, $\text{Co}(\text{II})\text{Co}(\text{III})$, or $\{\text{Co}(\text{III})\}_2$, the O can be the oxygen of oxo, hydroxo, or a water molecule, and the O_2 molecule may be superoxo or peroxy. The ligand field spectrum of the powdered compound indicates the presence of cobalt(III); however, due to strong charge-transfer absorptions the presence of $\text{Co}(\text{II})$ species cannot be totally excluded. UV-vis spectra of the cobalt compound in methanol (red solution) show a charge-transfer band of high intensity at $33.4 \times 10^3 \text{ cm}^{-1}$. No absorption at 14 kK is observed, indicating a peroxy

(8) Bouwman, E.; Driessen, W. L. *Synth. Commun.* **1988**, in press.

(9) Crystal data $[\text{Co}_2(\text{C}_{12}\text{H}_{18}\text{N}_4\text{S}_2)_2(\text{O}_2)(\text{OH})](\text{NO}_3)_3$, (μ -dioxxygen)(μ -hydroxo)bis[1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane]cobalt(III) tris(nitrate), $M_r = 917.73$, orthorhombic, space group $Pbcn$, $a = 12.20$ (1) Å, $b = 19.985$ (9) Å, $c = 15.980$ (8) Å, $Z = 4$, $D_x = 1.57 \text{ g cm}^{-3}$. A crystal ($0.34 \times 0.26 \times 0.30 \text{ mm}$) was sealed in an X-ray capillary for crystallographic studies. Function minimized is $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Final $R_f = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.0461$, final $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.0451$ for 1353 observed reflections with $I > 2\sigma(I)$ and $(\sin \theta/\lambda) > 0.30$. The positions of the cobalt ions were located in a Patterson map. The remaining atoms were easily found from subsequent Fourier maps. Refinements were carried out with use of anisotropic thermal parameters for all non-hydrogen atoms, except for two oxygens of the disordered nitrate ion. The estimated standard deviations in the distances and angles were established by using the full correlation matrix. Calculations were performed with crystallographic programs written or modified by Dr. R. A. G. de Graaff and E. Ruten-Keulemans on an IBM 3083 computer, with atomic scattering factors from the usual source.

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(4) Bedell, S. A.; Martell, A. E. *Inorg. Chem.* **1983**, *22*, 364.

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