ments. This caused us to examine alternate structures and in particular the interaction between a planar CH_2–C–CH_2 moiety and a $W_2(O\text{-}t\text{-}Bu)_6$ group.

The interaction diagram shown in Figure 1 emphasizes the close analogy between the μ-perpendicular alkyne[13,14] and the μ-perpendicular planar CH_2–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 nonbonding 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 $Cp_2Mo_2(CO)_4(C_3H_4)$[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 $W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}C_3H_4)$ thus may closely resemble that of the μ-alkyne and CO adducts of formula $M_2(OR)_6(\mu\text{-}X)$ where X = CO[15] or C_2R_2'.[16,17]

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An Unusual Dinuclear Cobalt Dioxygen Complex with a Tetradentate Thioether–Imidazole-Containing Ligand. Structure of $[Co_2(bidhx)_2(O_2)(OH)](NO_3)_3$

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Many dinuclear, dioxygen bridged cobalt(III) complexes are known.[1] Most of these dimers have the general formula $[N_4Co(O_2)(OH)CoN_4]^{n+}$, where N_4 corresponds to four nitrogen donor atoms, either bidentate (ethylenediamine[2]) or tetradentate (tris(2-aminoethyl)amine[3]). 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 dioxygen complexes is strongly determined by the nature of the N4 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 N4-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 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 dioxygen formed spontaneously, of which the synthesis and preliminary structure are described below.

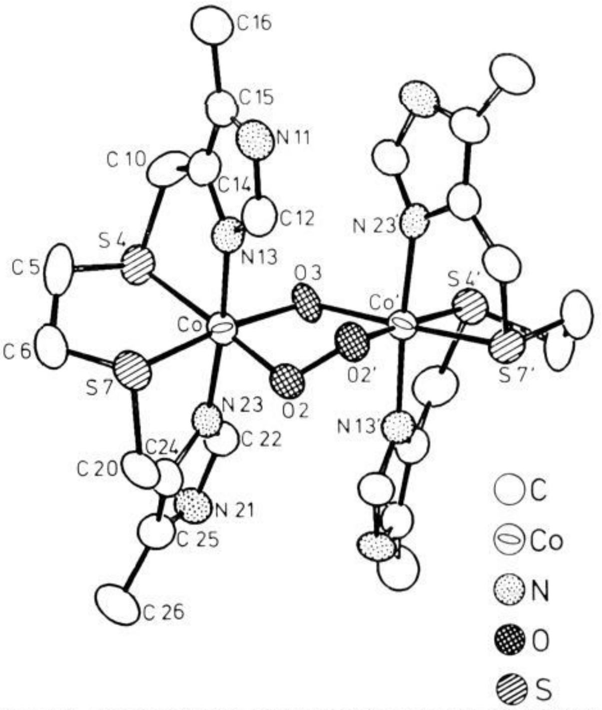

Figure 1. ORTEP projection of the dimeric cation $[Co_2(bidhx)_2(O_2)(OH)]^{3+}$, with thermal ellipsoids of 50% probability. The hydrogen atoms and the nitrate anions are omitted for clarity. The primed atoms are at the positions $1 - x, y, 0.5 - z$.

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 $Co_2(bidhx)_2(H_xO)(O_2)(NO_3)_3$ with x = 0, 1, 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 $(Co(II))_2$, Co(II)Co(III), or $(Co(III))_2$, the O can be the oxygen of oxo, hydroxo, or a water molecule, and the O_2 molecule may be superoxo or peroxo. The ligand field spectrum of the powdered compound indicates the presence of cobalt(III); however, due to strong charge-transfer absorptions the presence of Co(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 10^3 cm^{-1}. No absorption at 14 kK is observed, indicating a peroxo

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[9] Crystal data $[Co_2(C_{12}H_{18}N_4S_2)_2(O_2)(OH)](NO_3)_3$, ($\mu$-dioxygen)($\mu$-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 g cm^{-3}. A crystal (0.34 × 0.26 × 0.30 mm) was sealed in an X-ray capillary for crystallographic studies. Function minimized is $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Final $R_f = \Sigma(||F_o| - |F_c||)^2/\Sigma|F_o| = 0.0461$, final $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.0451$ 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. Rutten-Keulemans on an IBM 3083 computer, with atomic scattering factors from the usual source.

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group.[10] No EPR signal (spectra taken at room temperature and at 77 K) could be obtained from the powder nor from the ethanol solution, indicating that no unpaired electron is present in this compound, which excludes the presence of a superoxo species. This leaves two possible structural formulas for this compound viz. $[Co^{(II)}Co^{(III)}(bidhx)_2(H_2O)(O_2^{2-})]^{3+}$ or $[(Co^{(III)})_2(bidhx)_2(OH^-)(O_2^{2-})]^{3+}$ of which the latter seems the most likely.

The structure appeared to be incommensurate,[11] which was concluded from the high thermal anisotropy along the *b*-axis of all atoms. The structure was therefore refined with a reduced reflection set. The reflections with $(\sin \Theta/\lambda) < 0.30$ were omitted, which resulted in lower R_f and R_w values, and better standard deviations.

An ORTEP projection of the dimeric cation is shown in Figure 1. A twofold axis runs through the hydroxo group and the middle of the dioxygen molecule. For clarity the (disordered) nitrate anions have been omitted.

In $[Co_2(bidhx)_2(O_2)(OH)](NO_3)_3$ the ligand coordinates tetradentate, with the two imidazole nitrogens in axial positions. The two thioether sulfurs are cis coordinated with relatively short Co–S distances compared with other crystal structures with this and a similar ligand.[12,13] The two cobalt ions are bridged by a hydroxo group and a peroxo group thus completing the octahedral coordination sphere of the cobalt(III) ions.

The cobalt–dioxygen bond distance is 1.877 (6) Å, and the cobalt–hydroxo bond distance is 1.924 (5) Å, which is quite normal for this kind of compounds.[1] The distance between this hydroxy ion and one of the nitrate oxygens is 2.90 (2) Å, indicating the presence of a hydrogen bridge. Therefore, the O atom must be part of a hydroxy or a water molecule. The cobalt–sulfur coordination distances are 2.245 (2) and 2.302 (2) Å. These Co–S distances are rather short. Coordination compounds of divalent metals with the same ligand have metal–sulfur distances in the range of 2.5–2.8 Å.[9] However, other cobalt(III)–thioether complexes are known, in which the cobalt to sulfur distances are about 2.27 Å.[14] The cobalt–imidazole nitrogen distances are 1.919 (6) and 1.927 (5) Å, again rather short compared to other cobalt(III) imidazole compounds, where the distances vary from 1.95 to 2.05 Å.[15,16] The shorter distances, observed in the compound described here, are probably due to the chelating nature of the ligand.

The O–O bond distance is 1.38 (1) Å, which is quite short for a peroxo group when compared with the known structures of analogous compounds.[1] The average O–O bond distance reported for peroxo groups is about 1.46 Å, while the average O–O bond distance reported for bridging superoxo groups is 1.34 Å. The cobalt–dioxygen bond angle, however, is 110.9 (3)°, which is normal for peroxo coordination. The Co–O–O–Co torsion angle is 60.2°, which is also quite normal for doubly bridged dicobalt peroxo complexes.[17]

The study of the catalytic properties and other spectroscopic properties of this compound are in progress.

Acknowledgment. We are indebted to Prof. Dr. J. Reedijk for his stimulating interest in this study and to Dr. R. A. G. de Graaff for his assistance in the determination of the crystal structure.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and a full listing of bond lengths and bond angles (6 pages); tables of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Benz[*cd*]indazole: Infrared Spectroscopic Study

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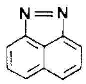
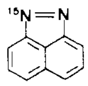
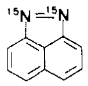
Benz[*cd*]indazole (**1**) is of interest as a simple heterocyclic system, and has been the subject of many unsuccessful synthetic attempts[1] before we (NCL group) succeeded in producing it by low-temperature photolysis of 1,8-diazidonaphthalene (**2**).[2] In our preliminary works, the first preparation of **1** has been characterized by UV-spectroscopy in an organic glassy matrix at 77 K from the photolysis of **2** and also by ^1H, ^{13}C, and ^{15}N NMR spectroscopies.[3,4] However, its detailed structural feature has still been ambiguous because it could not be isolated in the solid state at room temperature and was relatively stable only in dilute solution. We now report further structural information about **1** on the basis of the IR spectroscopic experiments in an argon matrix at cryogenic temperature.



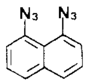
1



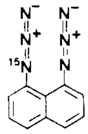
1a



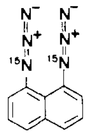
1b



2



2a



2b

For the IR spectroscopic study, two kinds of ^{15}N-labeled 1,8-diazidonaphthalenes (**2a** and **2b**), in addition to the unlabeled compound **1**, were prepared as precursors of **1a** and **1b**.[5] A mixture of 1,8-diazidonaphthalene (**2**, **2a**, or **2b**) and argon (1:200 to 1:500) was deposited on the CsI crystal plate at 20 K by the matrix isolation technique with a closed-cycle refrigerator system (Air Products CS 202). Photochemical changes upon the irradiation of **2**, **2a**, and **2b** with >300-nm light (through a UV-cut filter with a 500 W super-high-pressure mercury lamp) were followed by IR spectroscopy.

With the increase of irradiation time, the decrease of azido groups (N_3: 2100–2150 cm^{-1}) from the starting azide **2**[6] and the appearance of new peaks at 1450, 1285, 1232, 1220, 1210, 1198, 1168, 1150, 1025, 990, 978, 904, 814, 764, and 608 cm^{-1} werre observed (Figure 1a). These new peaks should be ascribed to **1**, because the corresponding UV spectrum of the sample prepared under the same conditions, as shown in Figure 2, was almost

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[6] The complete spectrum of **1** in an argon matrix at 20 K: 3076, 2272 (s), 2257 (s), 2197 (s), 2137 (s), 2122 (s), 2107 (s), 2092 (m), 2069 (m), 2054 (m), 1628 (m), 1601 (m), 1586 (m), 1579 (m), 1515, 1466, 1440, 1429, 1414, 1391 (s), 1376, 1361, 1342, 1327, 1316 (s), 1306, 1297 (s), 1170, 1155, 1102, 1023, 963, 817 (m), 794, 757 (m), and 689 (m) cm^{-1}.

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