Magnetic susceptibility measurements on powdered crystals of **2** between 299.7 and 5.2 K indicate that the metal ions are weakly coupled antiferromagnetically. The magnetic moment of the sample drops from 7.18 $\mu_B$/complex at 299.7 K to 0.872 $\mu_B$/complex at 5.2 K. Susceptibility data were least-squares fitted by using the Hamiltonian for an isotropic exchange interaction, $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ ($S_1$ and $S_2 = {}^5/_2$). The exchange-coupling constant $J$ was determined to be $-7.7$ cm$^{-1}$ with $g = 1.9$ and TIP fixed at $800 \times 10^{-6}$ cgsu. The powder EPR spectrum of **2** at 4.2 K is consistent with an $S = 5$ coupled binuclear system.[19]

In summary, the bimp$^-$ ligand appears capable of stabilizing heterobimetallic complexes containing discrete trivalent and divalent metal ion binding sites, similar to PAP and U$_f$. A complete discussion of the structure and properties of **2** and related complexes (Fe$^{III}$M$^{II}$, where M$^{II}$ = Co, Ni, Cu, and Zn) will be reported later. These complexes should be useful in evaluating the electronic properties of isolated iron centers in the presence or absence of exchange coupling.

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**Supplementary Material Available:** Figures displaying magnetic, Mössbauer, and EPR data and tables including atomic coordinates, isotropic and anisotropic thermal parameters, hydrogen coordinates, and bond lengths and bond angles (16 pages); a listing of structure factor amplitudes ($F_o$, $F_c$) (29 pages). Ordering information is given on any current masthead page.

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## Molecular Mechanics of Single Bonds in Tetrakis(carboxylato)dirhodium Systems

In a previous analysis[1] of dirhodium centers by molecular mechanics, a harmonic force constant of 0.88 mdyn Å$^{-1}$, calculated from a measured[2] Rh–Rh vibration frequency of 170 cm$^{-1}$, was used in the force field for Rh–Rh single bonds. More recent, more detailed electronic, infrared, Raman, and resonance Raman studies[3,4] have shown that $\nu$(Rh$_2$) should rather be assigned to the band at 289 cm$^{-1}$. It is of interest to see if this assignment could be sustained by molecular mechanics simulation of the known dirhodium systems, using the corresponding harmonic force constant of 2.73 mdyn Å$^{-1}$ (N cm$^{-1}$).

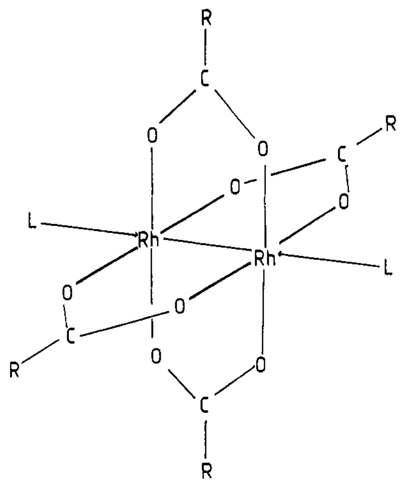

**Figure 1**. Schematic drawing of the bridged Rh$_2$(O$_2$CR)$_4$L$_2$.

**Table I**. Calculated and Observed Rh–Rh Distances ($k$ = 2.73 mdyn Å$^{-1}$) Together with the Tabulated Values of $r_0$

| axial donor, L | R | $r$(obs)/Å | ref | $r$(calc)/Å | $r_0$/Å |
|---|---|---|---|---|---|
| H$_2$O (planar) | CH$_3$ | 2.3855 (5) | 4 | 2.385 | 2.42 |
| H$_2$O (tetr) | CH$_3$ | 2.3855 (5) | 4 | 2.385 | 2.43 |
| Me$_2$OS | CH$_3$ | 2.406 (1) | 5 | 2.406 | 2.44 |
| Me$_2$OS | C$_2$H$_5$ | 2.407 (1) | 6 | 2.407 | 2.43 |
| Me$_2$SO | CF$_3$ | 2.419 (1) | 6 | 2.420 | 2.45 |
| H$_2$O (planar) | C(CH$_3$)$_3$ | 2.371 (1) | 5 | 2.371 | 2.41 |
| H$_2$O (tetr) | C(CH$_3$)$_3$ | 2.371 (1) | 5 | 2.371 | 2.42 |

**Table II**. Improved Force—Field Parameters for Bond Stretching ($k$/mdyn Å$^{-1}$, $r_0$/Å) and Angle Bonding ($k$/mdyn Å rad$^{-1}$, $\theta_0$/rad)

| | $k$ | $r_0$ or $\theta_0$ |
|---|---|---|
| Rh—S(ax) | 0.80 | 2.35 |
| H—O(ax) | 5.00 | 0.96 |
| C—S(ax) | 3.50 | 1.80 |
| O=S(ax) | 3.50 | 1.45 |
| O=C(br) | 3.00 | 1.26 |
| C—F | 0.40 | 1.32 |
| Rh—Rh—O,S(ax) | 0.3 | 3.1416 |
| O—Rh—O,S(br) | 0.8 | 1.571 |
| Rh—O—Lp(br) | 0.4 | 2.094 |
| Rh—O=C(br) | 0.2 | 2.094 |
| Lp—O=C(br) | 0.6 | 2.094 |
| O=C=O(br) | 1.5 | 2.094 |
| O=C(br)—C | 1.0 | 2.094 |
| F—C—C(br) | 0.65 | 1.911 |
| F—C—F | 0.52 | 1.911 |
| Rh—O—H,Lp(ax) | 0.4 | 2.094, 1.911 |
| Rh—S—C(ax) | 1.0 | 1.911 |

Torsional Parameters ($U$/J mol$^{-1}$, $\phi_0$/deg)

| | $U$ | $\phi_0$ |
|---|---|---|
| X—O=C—X | 0.63 | 0 |
| X—Rh—O—X(ax) | 0.42 | 90 |

Calculations were done on a series of Rh$_2$(O$_2$CR)$_4$L$_2$ systems,[5,6] shown in Figure 1, by using a Newton-Raphson minimization procedure coded by Boyd.[7] The series of compounds considered allowed for the variation of both the carboxyl group and the axial ligands. In each case the parameter $r_0$ in the expression for bond strain, $V = {}^1/_2k(r - r_0)^2$, was varied for constant $k$ = 2.73 mdyn Å$^{-1}$ until the observed bond length was reproduced. The results

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**Table III.** Buckingham Parameters for Nonbonded Interaction

| interacn | $a/10^5$ kJ mol$^{-1}$ | $b$/Å$^{-1}$ | $c/10^2$ Å$^6$ kJ mol$^{-1}$ |
|---|---|---|---|
| Rh···Lp | 0.26 | 3.13 | 7.05 |
| Rh···F | 1.30 | 3.44 | 11.4 |
| O···O | 15.2 | 4.62 | 15.2 |
| O···Lp,H | 3.74 | 4.58 | 5.36 |
| O···C | 21.2 | 4.61 | 15.2 |
| O···F | 6.16 | 4.62 | 8.43 |
| C···Lp,H | 5.31 | 4.57 | 5.49 |
| H,Lp···Lp,H | 1.06 | 4.55 | 2.07 |
| H,Lp···F | 1.49 | 4.59 | 2.78 |
| H,Lp···S | 2.29 | 3.94 | 13.1 |
| C···C | 30.3 | 4.60 | 15.2 |
| C···H | 5.31 | 4.57 | 5.49 |
| C···F | 8.32 | 4.61 | 8.19 |
| C···S | 13.1 | 4.05 | 32.4 |
| F···F | 2.73 | 4.63 | 4.91 |
| F···S | 7.58 | 4.22 | 20.6 |
| S···S | 17.8 | 3.80 | 84.3 |

are summarized in Table I. All the structures were simulated satisfactorily by using values of $r_0$ within the range 2.41–2.45 Å, which is considered to be within experimental error.

The conclusion to be drawn is that the Rh–Rh bond order is unity in all cases and that observed variations in bond length are due entirely to steric factors. The previous discussion[1] of these effects still apply. The only difference is the revised values for $(k, r_0)$ = (2.73 mdyn Å$^{-1}$, 2.43 Å). It is pointed out that any given molecular property can always be simulated in molecular mechanics by a matched pair of parameters $\{k, p_0\}$, consisting of a force constant and a characteristic value. In general, where neither is fixed by experimental evidence, a solution set can be chosen over an extensive range without affecting the simulation. The ultimate aim remains to have both parameters fixed experimentally for all bonds, but this objective is still to be achieved and easily frustrated by wrong assignments.

In the course of this study, we used the opportunity to improve on the previous force field for improved fit between observed and calculated structures. Modified parameters only are given in Tables II and III. We would like to thank Professor Robin Clark for drawing our attention to the new assignment of $\nu(Rh_2)$.

**Registry No.** $Rh_2(O_2CCH_3)_4(H_2O)_2$, 29998-99-0; $Rh_2(O_2CCH_3)_4(Me_2SO)_2$, 26023-60-9; $Rh_2(O_2CC_2H_5)_4(Me_2SO)_2$, 65507-56-4; $Rh_2(O_2CCF_3)_4(Me_2SO)_2$, 72665-42-0; $Rh_2(O_2CC(CH_3)_3)_4(H_2O)_2$, 70084-27-4; Rh, 7440-16-6.

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# Articles

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## Novel Vanadium(II) Amine Complexes: A Facile Entry in the Chemistry of Divalent Vanadium. Synthesis and Characterization of Mononuclear $L_4VCl_2$ [L = Amine, Pyridine]: X-ray Structures of *trans*-$(TMEDA)_2VCl_2$ [TMEDA = *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine] and *trans*-$Mz_2V(py)_2$ [Mz = *o*-$C_6H_4CH_2N(CH_3)_2$, py = Pyridine]

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Reaction of $[V_2(\mu\text{-}Cl)_3(THF)_6]_2[Zn_2Cl_6]$ with a slight excess of the nitrogen-containing ligand L [L = amine, pyridine] ruptured the bimetallic structure, allowing the large-scale preparation of the mononuclear high-spin V(II) derivatives *trans*-$L_4VCl_2$ [L = $^1/_2$ TMEDA (**1**), $^1/_2$ *N*,*N*,*N'*-trimethylethylenediamine (**2**), pyrrolidine (**3**), pyridine (**4**)] in crystalline form and good yield. Crystal data for **1** are as follows: monoclinic, $P2_1/n$, $a$ = 7.900 (3) Å, $b$ = 12.345 (5) Å, $c$ = 9.142 (3) Å, $\beta$ = 97.33 (3)°, $V$ = 884.3 (7) Å$^3$, $Z$ = 2. These complexes are versatile starting materials for the preparation of various V(II) complexes including the first dinitrogen derivative $[(py)(Mz)_2V]_2(\mu\text{-}N_2)$ (**5**) [Mz = *o*-$C_6H_4CH_2N(CH_3)_2$] and the monomeric aryl *trans*-$Mz_2V(py)_2$ (**6**). Crystal data for **6** are as follows: monoclinic, $P2_1/c$, $a$ = 9.990 (1) Å, $b$ = 15.536 (1) Å, $c$ = 16.369 (1) Å, $\beta$ = 95.17 (1)°, $V$ = 2530.2 (3) Å$^3$, $Z$ = 4.

### Introduction

During the past 10 years interest in the chemistry of low-valent vanadium has been attracted by several interesting features. Dinitrogen fixation/activation,[1] V–V multiple-bond formation,[2] strong reducing power,[3] and the puzzling role of the high concentration of vanadium in several living organisms[4] are all areas of active research. In spite of this wide interest, however, the chemistry of low-valent vanadium remains rather unknown, especially for oxidation state II,[5] information being available on mainly cyclopentadienyl[6] and related systems.[7] Undoubtedly the retarding factor in the development of this chemistry has been the lack of suitable V(II) starting materials. In fact, although

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