We also observed some spectra at lower temperatures (down to 95 K); the low-field line narrows and eventually structure begins to be resolved around $g_{eff} \simeq 4.3$ as expected from theory for the $S = {}^5/_2$ state.[3]

In summary, we have identified the broad low-field line in the room-temperature EPR spectra of several spin-crossover compounds as due to the $S = {}^5/_2$ state. The decrease in line intensity with decreased μ_{eff} is consistent with the decreased contribution from the $S = {}^5/_2$ state.

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Registry No. BBDF, 14526-32-0; MMDF, 60282-50-0; MBDF, 23674-41-1; ETDF, 35944-38-8; CPDF, 36763-00-5; CHDF, 21288-88-0.

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Molecular Structure of *trans*-Bis(benzeneselenido)[difluoro-3,3'-(trimethylenedinitrilo)bis(2-pentanone oximato)borate]rhodium(III)

James P. Collman,* Richard K. Rothrock, Judith P. Sen, Thomas D. Tullius, and Keith O. Hodgson

The development of new superconducting materials has aroused considerable interest among physicists and chemists. The speculative mechanism for superconductivity proposed by Little[1] suggests that "excitonic" interactions could result upon placing a one- or two-dimensional metal in the proximity of a readily polarizable medium. We are presently engaged in the synthesis and characterization of compounds comprised of a backbone of atoms of heavy elements covalently bound in a linear array. Our synthetic approach to this problem has centered about the oxidative addition of disulfides and diselenides to a square-planar, macrocyclic rhodium(I) complex. We wish to report here the x-ray crystal structure of a transition metal complex which serves as the simplest model for our future study in this area.

The oxidative addition of diphenyl diselenide to the square-planar [difluoro-3,3'-(trimethylenedinitrilo)bis(2-pentanone oximato)borate]rhodium(I),[2,3] **1** (commonly ab-

1

2
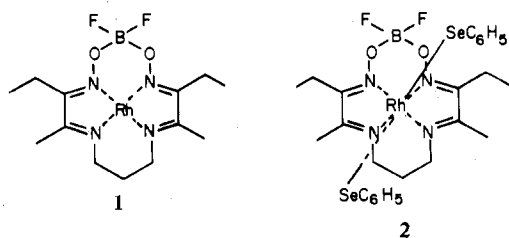
breviated as Rh[C$_2$(DO)(DOBF$_2$)]) affords the Rh(C$_2$(D-

Table I. Root-Mean-Square Amplitudes of Vibration

Atom	Axis 1	Axis 2	Axis 3	Atom	Axis 1	Axis 2	Axis 3
Rh	0.145	0.176	0.203	C13	0.170	0.246	0.301
Se1	0.173	0.198	0.270	C1P1	0.163	0.200	0.237
Se2	0.170	0.210	0.247	C2P1	0.184	0.239	0.259
N1	0.163	0.183	0.199	C3P1	0.175	0.233	0.336
N2	0.163	0.182	0.235	C4P1	0.180	0.215	0.370
N3	0.162	0.188	0.224	C5P1	0.196	0.255	0.337
N4	0.151	0.191	0.240	C6P1	0.202	0.241	0.262
C1	0.185	0.242	0.360	C1P2	0.186	0.202	0.221
C2	0.150	0.210	0.226	C2P2	0.170	0.192	0.244
C3	0.141	0.197	0.243	C3P2	0.168	0.228	0.276
C4	0.140	0.213	0.230	C4P2	0.181	0.251	0.334
C5	0.191	0.213	0.283	C5P2	0.132	0.265	0.361
C6	0.173	0.229	0.287	C6P2	0.180	0.233	0.291
C7	0.191	0.266	0.329	O1	0.166	0.201	0.313
C8	0.161	0.244	0.276	O2	0.185	0.196	0.292
C9	0.185	0.255	0.357	B	0.192	0.214	0.290
C10	0.175	0.237	0.259	F1	0.270	0.296	0.348
C11	0.167	0.180	0.227	F2	0.190	0.234	0.390
C12	0.165	0.176	0.258				

O)(DOBF$_2$)](SeC$_6$H$_5$)$_2$ complex, **2**. With respect to the oxidative addition reaction, the low-valent rhodium compound **1** is one of the most reactive d^8 transition metal complexes yet isolated. Substrates, including alkyl and acyl halides, alkyl tosylates, and alkyl and aryl disulfides and diselenides, generally undergo the addition by an S$_N$2 mechanism.[2]

Experimental Section

Preparation of Rh[C$_2$(DO)(DOBF$_2$)](SeC$_6$H$_5$)$_2$, 2. To a solution of Rh[C$_2$(DO)(DOFB$_2$)], **1**, (100 mg, 0.239 mmol), in dry tetrahydrofuran (10 ml) under a nitrogen atmosphere was added a tetrahydrofuran solution (5 ml) of diphenyl diselenide (80.0 mg, 0.256 mmol). After stirring of the solution for 1 h at room temperature, the solvent was removed under reduced pressure. The residue was recrystallized from acetonitrile affording ruby red crystals (110 mg, 62%). Ir (KBr pellet): ν_{CN} 1590, 1515 cm^{-1}; ν_{NO} 1112 cm^{-1}; ν_{BO} 1155, 808 cm^{-1}; ν_{BF} 995 cm^{-1}; ν_{Ph} 1562, 1450, 1424, 742, 690 cm^{-1}; ν_{Se-Ph} 467 cm^{-1}. NMR (60 MHz in CDCl$_3$): δ 1.00 (t, J = 8 Hz), 1.80 (s), 2.35 (q on m, J = 8 Hz), 4.00 (m), 7.20 (m). Anal. Calcd for C$_{25}$H$_{32}$BF$_2$N$_4$O$_2$RhSe$_2$: C, 41.12; H, 4.42; N, 7.67; Se, 21.63. Found: C, 41.14; H, 4.38; N, 7.52; Se, 21.60.

The compound crystallized as long, ruby red parallelepipeds, one of which was cleaved to a size (0.20 × 0.20 × 0.20 mm) suitable for diffraction studies. Data were collected on a Syntex P2$_1$ four-circle diffractometer equipped with a single-crystal graphite monochromator (Bragg 2θ angle 12.2°) using Mo K$\bar{\alpha}$ radiation ($\lambda_{K\bar{\alpha}}$ 0.710 73 Å) at a takeoff angle of 3.0°. Least-squares refinement of the setting angles of 15 machine-centered reflections resulted in parameters for a monoclinic unit cell of a = 15.361 (6) Å, b = 11.44 (1) Å, c = 16.374 (4) Å, β = 105.16 (4)°, and V = 2778 (4) Å^3. The crystal was found to belong uniquely to space group P2$_1$/c, with four molecules per unit cell (ρ_{calcd} = 1.75 g/ml; ρ_{obsd} = 1.73 g/ml, obtained by flotation in 1,2-dibromoethane/heptane).

Intensity data were collected employing variable-speed θ–2θ scans (2θ_{max} = 60°). A total of 8147 unique reflections ($h,k,\pm l$) were collected, of which 3659 had $|F_o|^2 > 3\sigma(|F_o|)^2$. Corrections were made for background and Lorentz–polarization. An absorption correction was not applied as the maximum and minimum values of μt for the very symmetric crystal vary only a few percent.

The coordinates of the Rh and one Se atom were determined from a three-dimensional Patterson map.[4] The positions of the other nonhydrogen atoms were determined by a subsequent difference Fourier. The structure was refined using full-matrix least squares where the function minimized was $\sum w(|F_o| - |F_c|)^2$ in which w is given by $4F_o^2/\sigma^2(F_o^2)$. The agreement factors R and R_w are defined as $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.

Including all nonhydrogen atoms with anisotropic temperature factors and fixed calculated H atom positions, the final values of R and R_w were both 0.052. The final error in an observation of unit weight was 1.66.

The rms amplitudes of vibration for all nonhydrogen atoms are given in Table I. [The observed and calculated structure factors are given in Table III and Table IV lists the positional and thermal parameters from the final refinement.[5]]
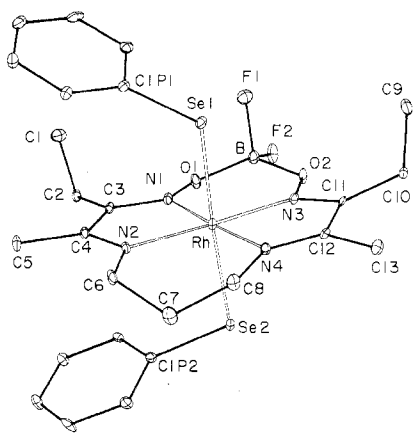
Figure 1. Perspective view of $Rh[C_2(DO)(DOBF_2)](SeC_6H_5)_2$ (5% probability ellipsoids) showing atomic numbering scheme. The hydrogen atoms have been omitted for clarity.

Table II. Bond Distances and Angles with Corresponding Estimated Standard Deviations

	Distances, Å		
Rh–Se1	2.510 (1)	Rh–N3	1.952 (5)
Rh–Se2	2.544 (1)	Rh–N4	1.978 (5)
Rh–N1	1.957 (5)	Se1–C1P1	1.927 (6)
Rh–N2	2.013 (5)	Se2–C1P2	1.926 (7)

	Angles, Deg		
Se1–Rh–Se2	174.69 (3)	N2–Rh–N4	102.83 (23)
N1–Rh–N2	79.04 (21)	N3–Rh–N4	79.74 (23)
N1–Rh–N3	98.35 (22)	Rh–Se1–C1P1	107.63 (24)
N1–Rh–N4	177.34 (22)	Rh–Se2–C1P2	105.01 (24)
N2–Rh–N3	177.08 (24)		

Description of the Structure

The crystal structure consists of discrete $Rh[C_2(DO)(DOBF_2)](SeC_6H_5)_2$ molecules with the configuration shown in Figure 1. Pertinent bond distances and angles are summarized in Table II.

The rhodium is surrounded by an octahedral ligand field and lies in the center of the plane of the four nitrogen atoms in the macrocycle, similar to the geometric environment observed in $[Co(CH_3)(H_2O)\{(DO)(DOH)\}]ClO_4$[6] and $Rh[C_2(DO)(DOBF_2)](CH_3)I$.[7] The Rh–N bond distances and angles in **2** are almost identical with those found for other $Rh[(DO)(DOBF_2)]$ related complexes[7,8] and are consistent with those in rhodium(III)–bis(dimethylglyoximato) complexes.[9] The Rh^{III}–N bond distances exceed those for the corresponding Co^{III}–N bond by an average of 0.1 Å.

The propylene bridge (C(6), C(7), C(8)) takes on a configuration such that C(7) lies below the plane of the macrocycle. Along a line diagonally projected through C(7) and Rh on the opposite side of the plane from C(7) lies the boron of the borate bridge. The overall conformation defined by C(7), B, and the four nitrogens resembles that of the "chair" conformer of cyclohexane.

The rigorous geometric demands of the square-planar, macrocyclic ligand give rise to the expected trans addition of the diselenide. This is borne out by the observed Se(1)–Rh–Se(2) bond angle of 174.69 (3)°. The constraint of the rhodium–selenium bonds to linearity by the chelating $C_2(DO)(DOBF_2)$ ligand indicates that this system offers a promising route toward the synthesis of one-dimensional intermetallic oligomers. In fact, we have more recently completed the synthesis of two larger, related oligomers, $Rh[C_2(DO)(DOBF_2)][XGe(C_6H_5)_3]_2$, X = S, Se.[10]

This is the first reported x-ray crystal structure of a rhodium complex containing an Rh–Se coordination bond. The Rh–Se distances in this complex are 2.510 (1) and 2.544 (1) Å, which may be compared with 2.49 Å, the sum of the covalent radii[11]

for Rh (1.32 Å) and Se (1.17 Å). Rhodium–sulfur distances in tris(dithioacetylacetonato)rhodium(III)[12] and tris(S-methylethene-1,2-dithiolato)rhodium(III)[13] fall in the range 2.31–2.37 Å.

Registry No. 1, 60224-26-2; **2**, 60224-27-3; diphenyl diselenide, 1666-13-3.

Supplementary Material Available: Listings of structure factors (Table III) and the positional and thermal parameters from the final refinement (Table IV) (19 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
The University of Michigan, Ann Arbor, Michigan 48109

Oxidation of 7-Thia-*nido*-undecaborate(2–) by Silver Ion to Give Arylthiaboranes

D. A. Thompson, W. R. Pretzer, and R. W. Rudolph*

Until it was shown that certain closo borane anions actually formed stable complexes[1] it was generally accepted that reduction of silver ion to silver metal was a useful confirmation of B–H bonds.[2] Even so, little is known regarding the fate of the borane moiety after oxidation by silver ion. Our work with boranes and heteroboranes and the redox nature of their interconversions[3–5] suggests oxidation by silver ion as a possible synthetic strategy. Here we report that oxidation of 7-$SB_{10}H_{10}^{2-}$ [6] by Ag^+ in benzene and toluene leads to coupled polyhedra and attack upon the solvent to give arylthiaboranes.[7]

Experimental Section

Reactions were carried out under a nitrogen atmosphere. Solvents were dried prior to use and were distilled in vacuo or under nitrogen. Toluene was dried under nitrogen by percolation through NaH using a Soxhlet extraction apparatus.

Synthesis of 2-(p-$CH_3C_6H_4$)-7-$SB_{10}H_{11}$. Thia-*nido*-undecaborate(2–) was generated in cyclohexane from 0.460 g (3.03 mmol) of 7-$SB_{10}H_{12}$ by addition of methyllithium according to the procedure