An analogous series of palladium complexes, $[Pd_2Cl_2(\mu\text{-}CO)(DPM)_2]$,[38] $[Pd_2Cl_2(\mu\text{-}SO_2)(DPM)_2]$,[39] and $[Pd_2Cl_2(\mu\text{-}HFB)(DPM)_2]$,[16] has also been structurally characterized and differs from the rhodium series most significantly in the absence of metal–metal bonds. Although not much of the chemistry of these species has been reported, it seems that the palladium complexes, which lack the metal–metal bonds, are less reactive than their rhodium counterparts.

The chemistry of $[Rh_2Cl_2(\mu\text{-}HFB)(DPM)_2]$ is now currently under investigation to see whether small molecules other than CO will insert into the Rh–Rh bond. In addition, since $[Pd_2Cl_2(\mu\text{-}HFB)(DPM)_2]$[16] was found to cyclotrimerize hexafluoro-2-butyne, the present species will also be tested as a cyclotrimerization catalyst.

Acknowledgment. We thank the University of Alberta and the Natural Sciences and Engineering Research Council of Canada for financial support and NSERC for a scholarship to R.S.D.

Registry No. **1**, 75503-68-3; **2**, 77590-00-2; $[RhCl(C_8H_{12})]_2$, 12092-47-6.

Supplementary Material Available: Listings of the idealized hydrogen parameters and the observed and calculated structure amplitudes (17 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Paramagnetic Properties of $[Ni(C_5H_5NO)_6](BrO_3)_2$

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The compound $[Ni(C_5H_5NO)_6](BrO_3)_2$ crystallizes in the space group $R\bar{3}$, with the metal atom at the center of the unit cell, which imposes a center of inversion and a threefold rotation axis at the metal atom. The coordination sphere of the nickel is rigorously octahedral; the unit cell parameters are $a = 9.513$ (1) Å and $\alpha = 84.58$ (1)°. The analysis of the susceptibilities measured at zero field yields the magnetic parameters $g_{\parallel} = 2.26 \pm 0.02$, $g_{\perp} = 2.33 \pm 0.02$, $D/k_B = 4.55 \pm 0.10$ K, and $zJ/k_B = -0.10 \pm 0.05$ K. The level-crossing field is found to be 31.0 kOe, and field-induced magnetic ordering in that external field is found not to occur down to at least 500 mK.

The magnetic properties of $S = 1$ spin-singlet ground-state systems have recently been of interest. The relevant compounds contain either trivalent vanadium[1-4] or divalent nickel[5-10] in sites of uniaxial symmetry. In the examples to which we refer, a spin doublet is found above a singlet, and the zero-field splitting of the two states is so much larger than the exchange interaction that magnetic ordering does not occur spontaneously in the absence of a parallel applied magnetic field. Because of the symmetry of the systems, an applied field can cause one component of the doublet to drop in energy, and a level crossing can thereby occur eventually. This puts a double degeneracy into the ground state of the system so that when the exchange interaction is also large enough and the temperature is low enough, magnetic ordering can occur. The first example of such a field-induced magnetic ordering was provided by $[Ni(C_5H_5NO)_6](ClO_4)_2$, where C_5H_5NO is pyridine *N*-oxide. Magnetic ordering occurs in this system at 0.75 K in an applied field of 48 kOe. The complete phase diagrams for this salt as well as the isostructural nitrate analogue have also been determined and have been found to be quite similar.[10] The subject has recently been reviewed.[11]

One of the fascinating sidelights of this research has been the discovery that the salts $[Ni(C_5H_5NO)_6]X_2$ are all found to be isostructural when X is ClO_4^-, BF_4^-, as well as NO_3^-. The iodide salt probably[12] is isostructural also. We now report the preparation, crystal structure, and susceptibility behavior of $[Ni(C_5H_5NO)_6](BrO_3)_2$. It has been found that the substitution of even the large bromate ion allows the integrity of the crystal lattice symmetry of this system to remain intact. Furthermore, the magnetic properties are found to be qualitatively similar to those of the other systems but differ interestingly in quantitative detail.

Experimental Section

Hydrated nickel bromate was prepared from reagent grade nickel sulfate and barium bromate. The pyridine *N*-oxide complex was prepared in the usual fashion.[13] Susceptibilities both at zero field and in an applied field have been measured in a fashion similar to that described earlier.[9] Our crystal structure analysis procedures have also been described.[14]

Crystal Data for $[Ni(C_5H_5NO)_6](BrO_3)_2$: $NiBr_2N_6O_{12}C_{30}H_{30}$, mol wt 885, space group $R\bar{3}$, $Z = 1$, $a = 9.513$ (1) Å, $\alpha = 84.58$ (1)°,

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Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $[Ni(C_5H_5NO)_6](BrO_3)_2$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.3798 (2)	0.3798 (2)	0.3798 (2)	5.9 (1)	5.9 (1)	5.9 (1)	−1.46 (8)	−1.46 (8)	−1.46 (8)
Ni	0.0	0.0	0.0	2.7 (1)	2.7 (1)	2.7 (1)	−0.3 (1)	−0.3 (1)	−0.3 (1)
O	0.3582 (7)	0.2192 (8)	0.4508 (8)	10.1 (5)	7.3 (4)	9.2 (4)	−0.6 (3)	−1.2 (3)	2.2 (3)
O(1)	0.2132 (4)	0.0260 (5)	−0.0407 (5)	2.4 (2)	3.6 (2)	3.9 (2)	−0.4 (2)	−0.3 (2)	0.4 (2)
N(1)	0.3038 (5)	−0.0440 (5)	0.0436 (5)	2.5 (2)	2.9 (2)	3.3 (2)	−0.1 (2)	−0.2 (2)	0.0 (2)
C(2)	0.3616 (7)	0.0271 (8)	0.1370 (8)	2.8 (3)	4.0 (3)	4.5 (3)	−0.1 (3)	−0.4 (2)	−1.2 (3)
C(3)	0.4574 (8)	−0.0406 (10)	0.2250 (8)	3.3 (3)	7.6 (5)	4.1 (3)	−0.5 (3)	−0.5 (3)	−1.4 (3)
C(4)	0.4941 (8)	−0.1806 (9)	0.2194 (8)	3.4 (3)	6.9 (5)	4.9 (4)	0.3 (4)	−1.4 (3)	1.6 (3)
C(5)	0.4341 (8)	−0.2531 (8)	0.1235 (9)	3.9 (3)	3.5 (3)	7.9 (5)	0.3 (3)	−1.8 (3)	0.2 (4)
C(6)	0.3392 (8)	−0.1819 (7)	0.0361 (8)	3.9 (3)	3.5 (3)	4.9 (4)	−0.1 (3)	−0.8 (3)	−0.9 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(2)	0.339 (7)	0.114 (7)	0.142 (7)	4 (2)	H(5)	0.466 (8)	−0.346 (7)	0.108 (7)	5 (2)
H(3)	0.499 (7)	0.000 (8)	0.297 (7)	5 (2)	H(6)	0.295 (7)	−0.225 (6)	−0.026 (7)	4 (1)
H(4)	0.559 (7)	−0.218 (8)	0.286 (8)	6 (2)					

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2)/4 + (B_{12}a^*b^*hk + B_{13}a^*c^*hl + B_{23}b^*c^*kl)/2]$.

Table II. Bond Lengths and Nearest Interionic Distances (Å)

Ni–O(1)	2.062 (3)	C(2)–C(3)	1.370 (8)
Br–O	1.634 (5)	C(3)–C(4)	1.350 (9)
O(1)–N(1)	1.323 (4)	C(4)–C(5)	1.387 (8)
N(1)–C(2)	1.351 (5)	C(5)–C(6)	1.373 (7)
N(1)–C(6)	1.330 (6)	⟨C–H⟩	0.91
O–C(3)	3.434 (6)[a]	O(1)–C(3)	3.452 (6)[c]
O–C(6)	3.453 (6)[b]	N(1)–C(3)	3.346 (6)[c]

[a] x, y, z. [b] $-y, -z, 1-x$. [c] $1-x, -y, -z$.

Table III. Bond Angles (Deg)

O(1)–Ni–O(1) $(R3)$[a]	90.1 (1)	C(2)–N(1)–C(6)	120.2 (4)
O(1)–Ni–O(1) $(R\bar{3})$	89.9 (1)	N(1)–C(2)–C(3)	121.0 (4)
O(1)–Ni–O(1)	180.0 (1)	C(2)–C(3)–C(4)	119.7 (5)
O–Br–O $(R3)$	104.5 (2)	C(3)–C(4)–C(5)	119.0 (5)
Ni–O(1)–N(1)	119.2 (2)	C(4)–C(5)–C(6)	119.9 (5)
O(1)–N(1)–C(2)	119.0 (3)	N(1)–C(6)–C(5)	120.3 (4)
O(1)–N(1)–C(6)	120.9 (4)		

[a] $R3$ and $R\bar{3}$ indicate oxygen atoms related by threefold rotation on the same side and on the opposite side of the inversion center, respectively.

$V = 850$ Å^3, $\rho_{obsd} = 1.69$ g cm^{-3}, $\rho_{calcd} = 1.73$ g cm^{-3}, μ(Mo Kα) = 26.7 cm^{-1}.

Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 52°$. Scan widths were calculated as $(A + B \tan \theta)$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.6 and 0.35°, respectively.

The intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and absorption. Of the 694 reflections collected, there were 465 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics. These data were used in the final refinement of the structural parameters.

Structure Determination. The nickel atom was assumed to be at the origin as in several other $[M(C_5H_5NO)_6]^{2+}$ complexes. The largest peak in the Patterson map calculated from all intensity data could then be interpreted as the Br atom and several other atoms could be similarly identified. The intensity data were phased sufficiently well by those positional coordinates to permit location of the other nonhydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[14] Anisotropic temperature factors were introduced for all nonhydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms which were included in the refinement for three cycles of least squares and then held fixed. The model converged with $R = 5.1$ and $R_w = 5.4$. A final Fourier difference function was featureless. Tables of the observed and calculated structure factors are available.[15] The principal programs used are as previously described.[14] The final positional and thermal parameters are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations, derived from the inverse matrix in the course of least-squares refinement calculations.

Results and Discussion

The nickel atom is located at the center of a perfect octahedron, as in the analogous $[Ni(C_5H_5NO)_6](NO_3)_2$. The six identical C_5H_5NO ligands have normal distances and angles. The nickel and bromine atoms lie on the threefold axis. Between each pair of nickel atoms, along the threefold axis, there are two BrO_3^- ions with their oxygen atoms eclipsed. In this regard, the complex resembles the nitrate analogue. Unlike the flat NO_3^- ligands, the two pyramidal BrO_3^- groups are like open umbrellas curved away from each other and toward the nickel atoms. This is shown in Figure 1.

The zero-field susceptibilities, measured parallel and perpendicular to the trigonal axis, are displayed in Figure 2. The data are similar to those observed for the other pyridine *N*-oxide compounds of nickel(II)[5,9] and may be analyzed in the same fashion. That is, the spin-Hamiltonian chosen is written as eq 1, for spin $S = 1$. A good fit to the data, as illustrated

$$\mathcal{H} = \mu_B \vec{H} \cdot \mathbf{g} \cdot \vec{S} + D[S_z^2 - \tfrac{1}{3}S(S+1)] \qquad (1)$$

by the solid curves in Figure 2, was obtained with the solutions of the above Hamiltonian but only after a subcritical molecular-exchange field correction was applied.[5,9] The parameters resulting are $g_\parallel = 2.26 \pm 0.02$, $g_\perp = 2.33 \pm 0.02$, $D/k_B = 4.55 \pm 0.10$ K, and $zJ/k_B = -0.10 \pm 0.05$ K, where the exchange correction is antiferromagnetic in sign.

These parameters are typical of those found with many nickel(II) salts but require some comment when a comparison is made with the other salts of the $[Ni(C_5H_5NO)_6]^{2+}$ ion. In particular, the zero-field splitting is similar to that observed with both the perchlorate (6.26 K)[5] and the nitrate (5.69 K)[9] salts, but nevertheless the value obtained here (4.55 K) is significantly smaller. This result was unexpected for the geometry of the $[Ni(C_5H_5NO)_6]^{2+}$ ion is virtually unchanged in the series of three salts. A change in zero-field splitting is usually explained in terms of changes in geometry of the magnetic ion.

Even more interesting is the fact that the subcritical exchange interaction parameter is at least 1 order of magnitude smaller in the bromate salt than that in the nitrate and perchlorate analogues. The analysis of the data in Figure 2 requires this result beyond question, and it is also in agreement with the field-dependent behavior of this material, which will now be described.

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(15) Supplementary material.

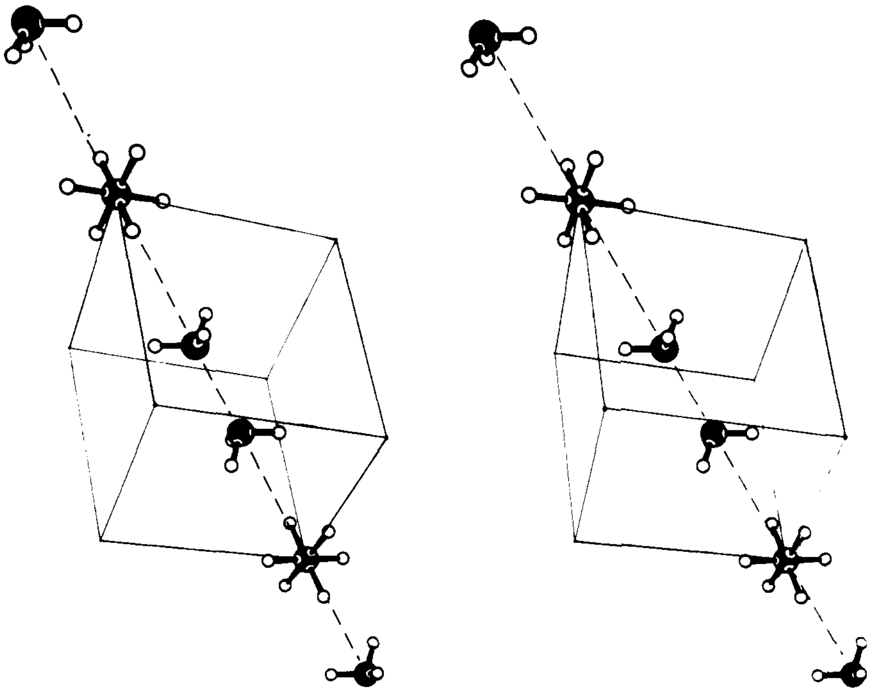

Figure 1. Ionic packing along the threefold (111) axis in the unit cell of $[Ni(C_5H_5NO)_6](BrO_3)_2$. The (111) axis is indicated by the dashed line. The pyridine groups are omitted for clarity.

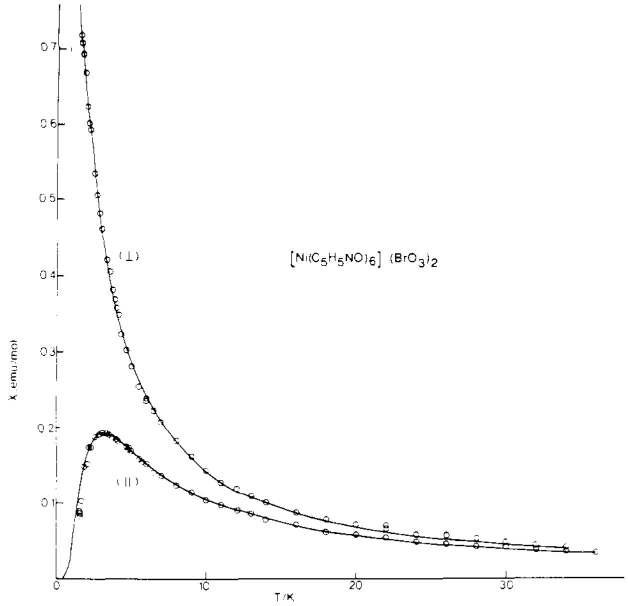

Figure 2. Susceptibilities parallel and perpendicular to the principal crystal axis. The points are experimental, and the curves were fitted as described in the text.

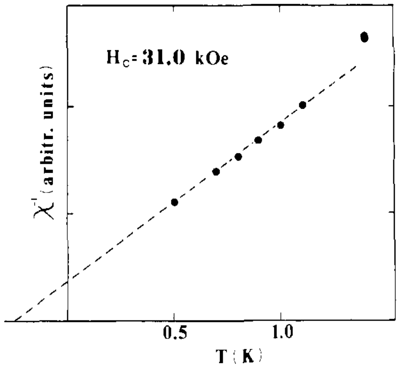

Figure 3. Inverse susceptibility as a function of temperature in a constant applied parallel field of 31.0 kOe.

The level-crossing field in $[Ni(C_5H_5NO)_6](NO_3)_2$ is about 42 kOe.[9] At this field, when it is applied parallel to the principal axis, magnetic ordering occurs at 0.899 K. As a consequence of the smaller zero-field splitting in the bromate salt, the observed level crossing field is found from measurements of the constant-temperature susceptibility as a function of applied field to be only $H_{\ell c} = 31.0$ kOe. The crossing field was identified as the applied field at which the susceptibility reaches its maximum value. And, as illustrated in Figure 3, $\chi_{\parallel}(H_{lc})$, the susceptibility measured as a function of temperature in the constant applied crossing field, obeys the Curie–Weiss law between 0.5 and 1 K with a Weiss constant of $\theta = -0.25$ K. That is, at the crossing field, $[Ni(C_5H_5NO)_6](BrO_3)_2$ remains paramagnetic down to at least 500 mK and probably to temperatures much lower than that. This is in marked contrast with the behavior of both the perchlorate and nitrate analogues. Thus, $[Ni(C_5H_5NO)_6](BrO_3)_2$ resembles magnetically $[C(NH_2)_3]V(SO_4)_2 \cdot 6H_2O$ more than its chemical isomorphs; the vanadium compound[4] also obeys the Curie–Weiss law at $H_{\ell c}$ between 0.5 and 1 K (with $\theta = -0.060$ K), and magnetic ordering in this compound has not yet been observed down to about 80 mK.

The reason for this result, an extraordinary diminution of the exchange interaction in the bromate compound when compared with the isostructural perchlorate and nitrate analogues, is not at all clear. Since the crystal structures are the same, the superexchange paths must be, by and large, the same. It is unlikely that the result is due to an increase in crystal lattice dimensions (resulting in a longer and therefore weaker superexchange path) since in fact the crystal lattice dimensions are quite similar: for the bromate, $a = 9.513$ Å, $\alpha = 84.58°$, and $V = 850$ Å^3; for the nitrate, $a = 9.486$ Å, $\alpha = 83.26°$, and $V = 837$ Å^3. Changes in crystal lattice dimensions of this magnitude caused changes in the exchange parameter of only about 10% in the case of the analogous cobalt salts.[12] The nickel ion is at the center of a perfect octahedron in each case. The Ni–O(1) distances are 2.067 (1) Å (NO_3^-) and 2.062 (3) Å (BrO_3^-), which differ insignificantly.

Another possible explanation is that the bromate ion is simply not as good a contributor to the superexchange path as either nitrate or perchlorate. We know of no other data in the literature which would allow us to prove or disprove that this may be the proper interpretation of the result, but we hesitate to believe that it will be an important part of the explanation. First of all, bromate ion is likely to be at least as polarizable ("soft") as nitrate or perchlorate ions and therefore at least as good a contributor to the superexchange path. Secondly, the counterions in these salts are only second-order contributors to the superexchange path anyway. The principal path, discussed earlier,[16] is of the form Ni–O- - -O–Ni, where the oxygens are from the pyridine *N*-oxide since the pyridine rings have moved out of the way. Again, with the cobalt analogues, the change in counterion is reflected only in small changes in the magnetic properties.[7]

That the nature of the superexchange path is as important for field-induced magnetic ordering as for the more usual examples of antiferromagnetic ordering was proved by recent studies[17] on $[Ni(thiourea)_4Cl_2]$. The superexchange path here is more favorable than that in the $[Ni(C_5H_5NO)_6]X_2$ series, and the ordering temperature at the level-crossing field is as high as 1.25 K.

The only explanation that occurs to us arises from the fact that the bromate ions are really pseudotetrahedral, with one of the positions being occupied by a stereochemically active lone pair of electrons. Perhaps the lone pairs interfere with the superexchange path in some fashion. In any case, in order to obtain more information on this question, it is intended to determine whether this is a general result by examining the magnetic ordering behavior of $[Co(C_5H_5NO)_6](BrO_3)_2$.

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Registry No. $[Ni(C_5H_5NO)_6](BrO_3)_2$, 77773-66-1.

Supplementary Material Available: Listing of observed and calculated structure factors (2 pages). Ordering information is given on any current masthead page.

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Iridium(I)–Salicylaldiminato–Cyclooctadiene Derivatives: Structural Features and Dynamic Behavior

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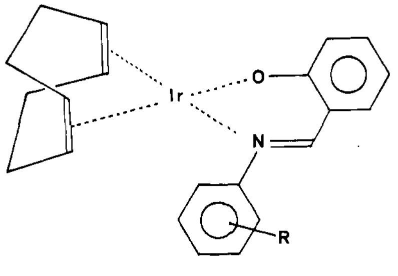
The reaction of $[(Ir(OCH_3)(cod))_2]$ (cod = 1,5-cyclooctadiene) with bidentate Schiff base (sb) derived from salicylaldehyde (sal) gives compounds of the general formula [Ir(sb)(cod)]. The structure of one complex of this type has been solved by X-ray diffraction techniques in order to explain the ^{13}C NMR spin–lattice relaxation time (T_1) studies. The complex [Ir(sal=N-*o*-tol)(cod)] crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 10.776$ (4) Å, $b = 9.882$ (2) Å, $c = 19.554$ (5) Å, $\beta = 118.06$ (3)°, $V = 1837.5$ Å^3, and $D_{calcd} = 1.84$ cm^{-3} for mol wt 510.6 and $Z = 4$. Diffraction data were collected with an Enraf-Nonius CAD-4 diffractometer, and the structure was solved and refined via a combination of Patterson, difference Fourier, and full-matrix least-squares techniques. The final discrepancy indices are $R = 0.043$ and $R_w = 0.044$ for 3417 independent reflections with $2\theta \leq 60°$ (Mo Kα radiation). Important bond lengths are Ir(I)–N = 2.099 (9) Å, Ir(I)–O = 2.004 (8) Å, and Ir(I)–C(olefin) = 2.05 (1)–2.16 (1) Å. The salicylidene moiety (ring A) is approximately perpendicular to the *o*-tolyl group (ring B). Comparison between the ^{13}C spin–lattice relaxation times (T_1) of ring A and ring B of a series of complexes with different B rings shows that any rotation of this latter ring is excluded. Only a small tumbling of ring B is assumed.

Introduction

A considerable number of compounds containing salicylaldiminato ligands have been examined; however, these investigations are mostly devoted to complexes of the first-row transition metals. As a part of our continuing interest in the coordination chemistry of iridium(I) and rhodium(I) compounds with 1,5-cyclooctadiene as the chelating ligand, we have synthesized some derivatives [M(sb)(cod)], where M = Ir(I) and Rh(I), cod = 1,5-cyclooctadiene, and sb = Schiff base derived from salicyaldehyde.

Discussion will center on molecule **1**. The Schiff bases are prepared by condensation of salicylaldehyde and the appropriate aromatic amines. The abbreviations utilized hereafter are listed in Table I.



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The donor–acceptor properties of central metal atom are altered by the ortho or meta substituent of the phenyl group of the Schiff base ligand. The changes in ^1H or ^{13}C nuclear magnetic resonance shifts of the double bond of the olefin moiety appear to be a sensitive probe of metal to ligand bonding.[2-3] In order to elucidate the spectroscopic results and

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