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 $[Co(C_5H_5NO)_6](BrO_3)_2$.

Acknowledgment. This research was supported in Chicago by the National Science Foundation under Grants DMR 76-18963 and DMR 7906119 and in Charlottesville by Grant CHE 77-01372 and by the CNPq (Brazil).

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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Contribution from the Laboratoire de Cinétique Chimique, Université Pierre et Marie Curie, 75005 Paris, France,
and Groupe de Mesures Spectrochimiques, Laboratoire de Chimie Organique Structurale,
ERA No. 557, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

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

R. BONNAIRE,*[1a] J. M. MANOLI,[1a] C. POTVIN,[1a] N. PLATZER,[1b] and N. GOASDOUE[1b]

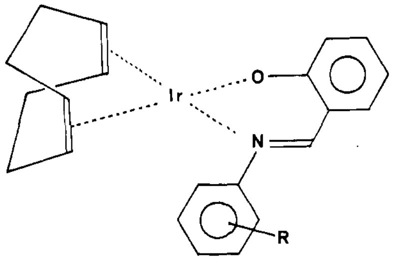
Received October 23, 1980

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.



1

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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[1] (a) Laboratoire de Cinétique Chimique. (b) Laboratoire de Chimie Organique Structurale.

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Table I. List of the Abbreviations for **1**

R = H	[Ir(salanil)(cod)]
R = 2-CH_3	[Ir(sal-*o*-tol)(cod)]
R = 3-CH_3	[Ir(sal-*m*-tol)(cod)]
R = 4-C_6H_5	[Ir(salabp)(cod)]

to make an unequivocal choice among the various structural possibilities envisaged, we decided to solve the structure of the complex [Ir(sal-*o*-tol)(cod)]. Furthermore we report on the use of ^{13}C spin-lattice relaxation time (T_1) measurements as a tool for obtaining information about possible motion of the phenyl group of the salicylaldiminato moiety.

Experimental Section

Materials. For the Schiff base synthesis, all reagents were obtained from commercial sources, with salicylaldehyde and the liquid aromatic amines being purified by distillation under vacuum. All solvents used in the synthesis were Analytical grade reagents and all reactions were carried out under a nitrogen atmosphere. The compound [(Ir(OCH_3)(cod))$_2$] used for the synthesis of the complexes was prepared as previously described.[4]

Preparation of the Ligands. The Schiff base ligands were prepared by reaction of equivalent amounts of salicylaldehyde and of the appropriate amine in hot methanol. The reaction mixture was concentrated and then cooled until precipitation of the ligand occurred. The powdered material obtained was filtered, washed with cold methanol, and dried under vacuum.

Preparation of the Metal Complexes [Ir(sb)(cod)]. The solid [(Ir(OCH_3)(cod))$_2$] compound and the appropriate ligand was dissolved in dichloromethane after which the solution was concentrated by boiling under nitrogen. Evaporated dichloromethane was progressively replaced by pentane, and the reaction mixture was cooled until the compound precipitated. The solid obtained was vacuum filtered, washed with pentane, and dried under vacuum. Quantitative analysis gave satisfactory results.

Physical Measurements. ^{13}C NMR spectra were recorded on a JEOL PS 100 in the Groupe de Mesures physiques de Paris Centre. The observation frequency of carbon-13 was 25.15 MHz, the 90° pulse was 25 μs, and the temperature was 25 °C.

The compounds were dissolved in $CDCl_3$, the solutions being carefully degassed by four freeze–pump–thaw cycles. T_1 values for protonated carbon atoms were measured by the inversion recovery method $(80°–\tau–90°–5T_1)_n$. The Overhauser effect was measured directly by using pulse modulated wide-band proton decoupling. Pulse intervals were at least $5T_1$.

Single-Crystal X-ray Data Collection. An X-ray single-crystal analysis was carried out on the [Ir(sal-*o*-tol)(cod)] complex. Slow diffusion at 5 °C of methanol into a concentrated dichloromethane solution of the complex yielded orange crystals suitable for X-ray diffraction.

Monoclinic symmetry was indicated by a photographic study using Weissenberg and precession cameras, and preliminary cell constants were obtained. Systematic absences *k* odd for 0*k*0 and *l* odd for *h*0*l* uniquely define the space group as $P2_1/c$ (C_{2h}^5, No. 14).

A well-formed prismatic crystal of approximate dimensions 0.39 × 0.21 × 0.15 mm was selected for data collection, mounted on the end of a glass fiber, and transferred to an Enraf-Nonius CAD-4 diffractometer.

Accurate cell parameters and orientation matrix were determined by least-squares refinement of the setting angles of 21 reflections. Cell constants are a = 10.776 (4) Å, b = 9.882 (2) Å, c = 19.554 (5) Å, and β = 118.06 (3)°. On the assumption of 4 formula units per cell, the calculated density, D_c = 1.84 g cm^{-3}, is in satisfactory agreement with the experimental one, D_m = 1.82 g cm^{-3}, measured by flotation in a $ZnBr_2$ aqueous solution.

Data were collected by using θ–2θ scans and graphite-monochromatized Mo Kα radiation to θ = 30°. The scan width was calculated according to the formula SW = 0.80 + 0.35 tan θ and was extended by 25% on each end of scan range for background measurement in a way previously described.[5] The intensity of three standard reflections (400, 040, 008) were monitored at intervals of 100 reflections and show no systematic trends. The data were processed by using an ignorance factor p of 0.03 in the estimation of standard deviations. Among the 5174 independent reflections collected, 3417 were measured above zero and were used in the final refinement.

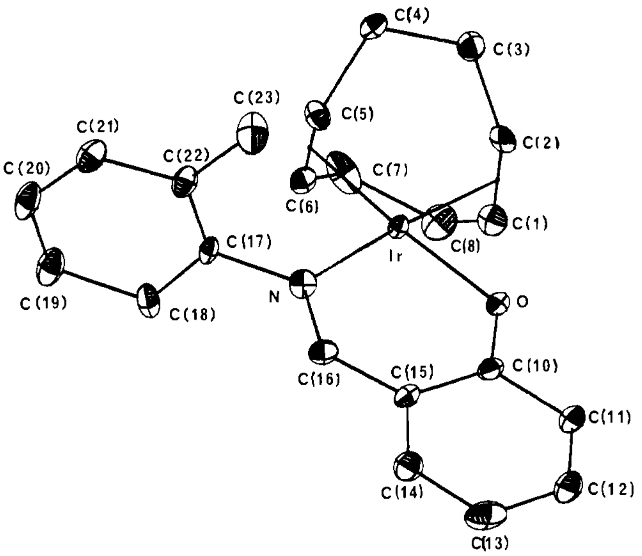

Figure 1. Perspective representation of [Ir(sal-*o*-tol)(cod)]. The vibrational ellipsoids are drawn at the 50% probability level. The labeling scheme is also shown.

On the basis of a linear absorption coefficient of 41.80 cm^{-1}, the resultant transmission factors ranged from 0.200 to 0.481; consequently absorption corrections were applied by using a numerical method.[6]

Structure Determination

Refinement of the structure was effected by full-matrix least-squares techniques. Throughout the refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are observed and calculated structure amplitudes and the weight w is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices R and R_w are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{0.5}$. The atomic scattering factors for all atoms and anomalous terms for the iridium atom are from the usual source.[7]

The atomic coordinates of the iridium atom were derived from a three-dimensional Patterson synthesis. The remaining nonhydrogen atoms were located by successive difference Fourier maps and least-squares refinements. At this point a least-squares refinement using anisotropic thermal parameters was performed. The values of R and R_w were 0.047 and 0.056, respectively.

All the hydrogen atoms were determined on the ensuing Fourier difference maps. Only the positional parameters of the methyl hydrogen atoms were allowed to refine; all others were not refined but included in the calculations in idealized positions (assuming the appropriate geometries and a C–H distance of 0.95 Å). The thermal parameter for a given hydrogen atom was arbitrarily taken as 6 Å^2 and was kept fixed.

The final refinement converged to values of R and R_w of 0.043 and 0.044, respectively, and to an error in observation of unit weight of 0.525 e for 235 variables and 3417 observations.

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Table II. Positional and Thermal Parameters[a, b] for the Atoms of [Ir(sal-*o*-tol)(cod)]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ir	0.29195 (5)	0.47809 (5)	0.63266 (3)	70.5 (3)	68.6 (4)	24.3 (1)	−2.6 (5)	25.2 (2)	−0.9 (4)
C(1)	0.4240 (13)	0.6329 (14)	0.6233 (9)	119 (18)	96 (18)	40 (7)	−41 (14)	35 (9)	8 (8)
C(2)	0.4950 (11)	0.5720 (11)	0.6983 (8)	74 (12)	71 (13)	38 (6)	−41 (10)	18 (7)	−26 (7)
C(3)	0.5165 (13)	0.6296 (14)	0.7715 (8)	107 (11)	129 (18)	41 (7)	−12 (14)	33 (9)	−14 (9)
C(4)	0.3985 (13)	0.6057 (15)	0.7906 (7)	120 (17)	170 (21)	27 (5)	9 (15)	36 (8)	2 (8)
C(5)	0.2596 (11)	0.5608 (12)	0.7190 (7)	75 (13)	101 (17)	34 (5)	13 (11)	16 (7)	11 (7)
C(6)	0.1943 (12)	0.6488 (13)	0.6547 (8)	104 (16)	74 (15)	34 (6)	2 (20)	30 (8)	−20 (7)
C(7)	0.2540 (13)	0.7820 (14)	0.6477 (11)	109 (20)	67 (16)	76 (11)	−8 (13)	18 (11)	7 (10)
C(8)	0.3495 (16)	0.7669 (16)	0.6077 (10)	193 (25)	122 (23)	53 (8)	−16 (19)	59 (12)	15 (11)
O	0.3751 (8)	0.3651 (9)	0.5793 (5)	85 (10)	156 (14)	25 (4)	−17 (9)	27 (5)	−13 (6)
N	0.1237 (10)	0.3418 (8)	0.5978 (6)	105 (12)	34 (10)	35 (5)	−4 (8)	30 (6)	0 (5)
C(10)	0.3198 (12)	0.2590 (13)	0.5343 (7)	101 (15)	97 (17)	19 (4)	25 (12)	22 (7)	3 (7)
C(11)	0.3964 (13)	0.2031 (16)	0.4978 (8)	114 (17)	145 (22)	33 (6)	21 (15)	34 (9)	−12 (9)
C(12)	0.3451 (15)	0.0938 (17)	0.4512 (9)	143 (20)	192 (26)	46 (7)	51 (18)	45 (10)	−19 (11)
C(13)	0.2127 (18)	0.0370 (16)	0.4323 (8)	238 (26)	114 (21)	39 (6)	10 (20)	38 (11)	−28 (10)
C(14)	0.1408 (13)	0.0913 (15)	0.4682 (9)	127 (18)	116 (20)	38 (6)	16 (14)	32 (9)	−8 (9)
C(15)	0.1878 (12)	0.1988 (12)	0.5172 (7)	109 (15)	74 (15)	23 (4)	12 (11)	30 (7)	2 (6)
C(16)	0.1040 (11)	0.2418 (12)	0.5497 (7)	113 (16)	71 (15)	27 (5)	−4 (12)	24 (7)	−5 (7)
C(17)	0.0177 (11)	0.3566 (11)	0.6239 (7)	78 (13)	73 (14)	32 (5)	−9 (10)	36 (7)	−3 (7)
C(18)	−0.0995 (11)	0.4297 (12)	0.5736 (8)	72 (13)	107 (17)	53 (7)	3 (11)	30 (8)	−10 (9)
C(19)	−0.2098 (14)	0.4406 (14)	0.6008 (10)	155 (20)	106 (21)	64 (8)	−33 (15)	72 (11)	−11 (10)
C(20)	−0.1946 (15)	0.3815 (16)	0.6630 (11)	153 (21)	122 (21)	66 (9)	−48 (17)	78 (12)	−23 (11)
C(21)	−0.0763 (15)	0.3083 (14)	0.7085 (9)	167 (21)	95 (17)	44 (7)	1 (15)	58 (10)	10 (9)
C(22)	0.0331 (13)	0.2974 (13)	0.6881 (8)	122 (17)	87 (16)	40 (6)	8 (12)	47 (9)	10 (8)
C(23)	0.1595 (21)	0.2098 (27)	0.7387 (13)	158 (29)	202 (32)	62 (9)	64 (25)	58 (14)	72 (15)

atom	x	y	z	atom	x	y	z
H(1)[c]	0.426	0.582	0.578	H(11)	0.487	0.244	0.505
H(2)	0.532	0.482	0.700	H(12)	0.402	0.053	0.429
H(3A)	0.603	0.594	0.812	H(13)	0.179	−0.039	0.395
H(3B)	0.529	0.725	0.770	H(14)	0.053	0.049	0.456
H(4A)	0.427	0.535	0.831	H(16)	−0.176	0.190	0.533
H(4B)	0.382	0.685	0.814	H(18)	−0.182	0.485	0.562
H(5)	0.214	0.475	0.719	H(19)	−0.291	0.496	0.568
H(6)	0.105	0.623	0.613	H(20)	−0.271	0.390	0.675
H(7A)	0.179	0.844	0.619	H(21)	−0.072	0.265	0.755
H(7B)	0.310	0.819	0.699	H(23A)	0.209 (22)	0.243 (24)	0.716 (17)
H(8A)	0.292	0.777	0.551	H(23B)	0.228 (28)	0.206 (25)	0.776 (13)
H(8B)	0.419	0.838	0.622	H(23C)	0.200 (15)	0.103 (16)	0.716 (9)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The components of the anisotropic temperature factors have been multiplied by 10^4. [b] For all hydrogen atoms $B = 6.00$ Å^2. [c] Number refers to carbon atom to which the hydrogen is bonded.

The highest peaks in the final difference Fourier map were located in the vicinity of the iridium atom. The rest of the peaks are featureless.

The observed and calculated structure amplitudes and the derived root-mean-square amplitudes of vibration are available as supplementary material. Refined atomic parameters are listed in Table II.

Results and Discussion

The crystal structure of [Ir(sal-*o*-tol)(cod)] consists of well-separated arrays of discrete molecular units, the only nonhydrogen intermolecular separation less than 3.5 Å being O···C(3) = 3.47 Å.

Figure 1 provides a perspective view of the complex together with the labeling scheme. Intramolecular distances and angles are compiled in Table III.

The geometry around the iridium atom is approximately square planar with the coordination polyhedra defined by the oxygen and nitrogen atoms of the Schiff base ligand and the midpoints[8] of the two olefinic bonds of the 1,5-cyclooctadiene ring. A least-squares plane (Table IV) consisting of Ir, N, O, M(1), and M(2) was calculated and showed no atom more than 0.012 Å out of the mean plane.

The "bite" angle O–Ir–N (90.2 (4)°) is in agreement with similar angles found in related mononuclear complexes with the salicylaldiminato group and presenting an approximately square-planar configuration at the central atom.[9]

The "bite" angle M(1)–Ir–M(2) of 88.0° containing the olefin bonds of cod deviates slightly from square geometry. This value is greater than those found in other iridium complexes with cod: 83.2–86.6°;[10] however, these reported complexes have a distorted trigonal-bipyramidal geometry around iridium(I).

The Ir–N bond length is 2.099 (3) Å while the Ir–O bond distance is only 2.004 (8) Å. The Ir–C distances are different for one double bond (2.05 (1) and 2.14 (1) Å) and equal (2.16 (1) Å) for the other. Furthermore the Ir–M(2) distance of 1.97 (2) Å for the former C═C opposite to the O atom is shorter than for the latter (Ir–M(1) = 2.032 (2) Å). This difference is not significant (only 2 esd) to indicate anything about the trans influences of the oxygen and nitrogen atoms.

The coordinated 1,5-cyclooctadiene takes its customary "tub" conformation. The coordinated double bonds C(1)–C(2) and C(5)–C(6) have lengths of 1.43 (2) and 1.41 (2) Å, respectively, compared to an uncoordinated olefinic distance of 1.34 Å.[11] Variations in the lengths of coordinated C═C bonds are expected to arise according to the Dewar–Chatt–Dun-

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(8) M(1) is the midpoint of C(1)–C(2); M(2) is the midpoint of C(5)–C(6).

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Table III. Interatomic Distances (Å) and Angles (Deg)

	Iridium-Ligand Bond Lengths		
Ir-O	2.004 (8)	Ir-M(1)	2.034 (14)
Ir-N	2.099 (9)	Ir-M(2)	1.970 (16)
	Distances within cod Fragment		
C(1)-C(2)	1.429 (18)	C(4)-C(5)	1.557 (16)
C(1)-C(8)	1.504 (20)	C(5)-C(6)	1.415 (17)
C(2)-C(3)	1.455 (18)	C(6)-C(7)	1.498 (18)
C(3)-C(4)	1.502 (17)	C(7)-C(8)	1.565 (21)
	Distances in Salicylaldiminato Residue		
O-C(10)	1.317 (14)	C(13)-C(14)	1.374 (18)
C(10)-C(15)	1.429 (15)	C(14)-C(15)	1.359 (17)
C(10)-C(11)	1.432 (16)	C(15)-C(16)	1.392 (15)
C(11)-C(12)	1.352 (19)	C(16)-N	1.311 (14)
C(12)-C(13)	1.411 (20)		
	Distances in Tolyl Moiety		
C(17)-N	1.460 (13)	C(19)-C(20)	1.287 (19)
C(17)-C(18)	1.383 (15)	C(20)-C(21)	1.369 (19)
C(17)-C(22)	1.323 (16)	C(21)-C(22)	1.414 (16)
C(19)-C(18)	1.518 (18)	C(22)-C(23)	1.522 (20)
C(23)-H(23A)	0.90 (21)	C(23)-H(23C)	1.30 (16)
C(23)-H(23B)	0.76 (25)		
	Angles about Iridium Atom		
N-Ir-O	90.2 (4)	M(1)-Ir-M(2)	88.0 (6)
N-Ir-M(2)	96.4 (5)	O-Ir-M(1)	85.4 (5)
	Angles within cod Fragment		
C(1)-C(2)-C(3)	127 (1)	C(5)-C(6)-C(7)	124 (1)
C(2)-C(3)-C(4)	115 (1)	C(6)-C(7)-C(8)	112 (1)
C(3)-C(4)-C(5)	113 (1)	C(7)-C(8)-C(1)	113 (1)
C(4)-C(5)-C(6)	119 (1)	C(8)-C(1)-C(2)	124 (1)
	Angles in Salicylaldiminato Residue		
Ir-O-C(10)	128.2 (7)	Ir-N-C(16)	122.7 (8)
O-C(10)-C(11)	125 (1)	C(12)-C(13)-C(14)	117 (1)
O-C(10)-C(15)	117 (1)	C(13)-C(14)-C(15)	124 (1)
C(10)-C(11)-C(12)	120 (1)	C(14)-C(15)-C(10)	119 (1)
C(11)-C(12)-C(13)	122 (1)	C(14)-C(15)-C(16)	117 (1)
	Internal Angles of Tolyl Ring		
N-C(17)-C(18)	114 (1)	C(20)-C(21)-C(22)	120 (1)
N-C(17)-C(22)	121 (1)	C(21)-C(22)-C(17)	119 (1)
C(17)-C(18)-C(19)	113 (1)	C(22)-C(17)-C(18)	125 (1)
C(18)-C(19)-C(20)	122 (1)	C(23)-C(22)-C(21)	118 (1)
C(19)-C(20)-C(21)	121 (1)	C(23)-C(22)-C(17)	123 (1)
C(16)-N-C(17)	115.9 (9)	Ir-N-C(17)	121.4 (7)

canson model for olefin bonding.[12-14] The C–C distances and angles in the cod group are within experimental range of their normal values.[10,15]

The C=C double bonds are not coordinated perpendicular to the Ir–M(1)–M(2) plane but are tilted in an opposite direction by 7.5° for C(1)–C(2) and 8° for C(6)–C(5), respectively.

The nine atoms of the salicylaldiminato fragment, O, N, C(16), and C(10)–C(15), all lie in a plane (Table IV), the maximum distance of any atom from the calculated least-squares plane being 0.034 Å.

The bond lengths and angles in the salicylaldiminato ligand are equal within experimental error to those reported in molecules containing similar ligands. The O–C(10) bond (1.317 (14) Å) is significantly longer than ketonic bonds; a lengthening of the N–C(16) bond (1.311 (14) Å) is also observed with respect to the double N=C bonds. It seems likely to explain these values of the ligand bond lengths in terms of π-electron delocalization on the whole planar bidentate ligands.[17] Such variations in bond lengths are also observed in other square-planar structures.[9]

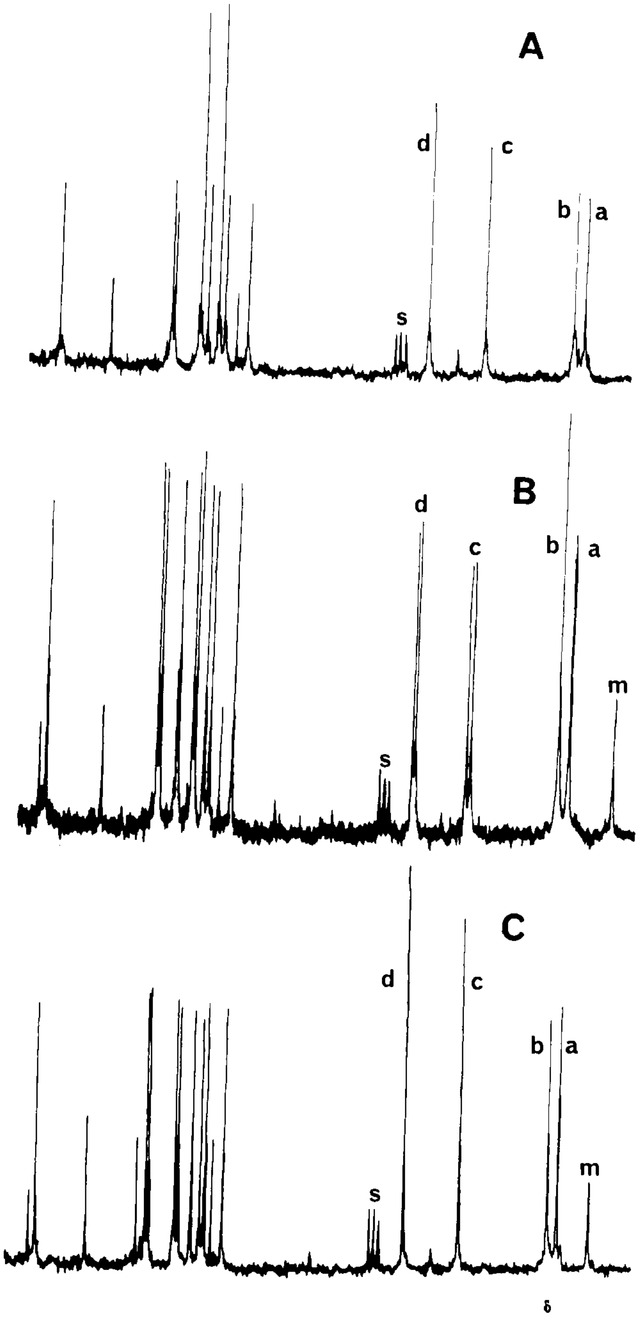

Figure 2. ^{13}C NMR spectra of [Ir(sb)(cod)] in $CDCl_3$ at 25 °C: (A) [Ir(salanil)(cod)]; (B) [Ir(sal-*o*-tol)(cod)]; (C) [Ir(sal-*m*-tol)(cod)]. Labels: a, CH_2 of cod trans to O; b, CH_2 of cod trans to N; c, =C—H of cod trans to O; d, =C—H of cod trans to N; m, methyl group; s, solvent. Other signals are assigned to the Schiff base ligand.

The *o*-tolyl group shows no significant deviation from planarity (maximum distance of any atom to the least-squares plane 0.029 Å). The dihedral angle between the *o*-tolyl plane and the salicylaldiminato residue is 85.65°. Table V reports the corresponding dihedral angle observed in other similar complexes and in free ligands where the substituent on the

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Table IV. Equations of Least-Squares Planes and Distances (Å) of Individual Atoms Defining the Planes from the Planes[a]

Coordination Plane					
Plane 1: $-0.1346x + 0.5157y - 0.8461z = -6.4290$					
Ir	−0.012	N	0.003	O	0.003
M(1)	0.003	M(2)	0.003		
Salicylaldiminato Group					
Plane 2: $-0.1226x + 0.6213y - 0.7739z = -5.3620$					
C(10)	−0.004	C(11)	−0.002	C(12)	−0.035
C(13)	0.021	C(14)	0.012	C(15)	0.009
C(16)	−0.013	O	0.023	N	−0.012
o-Tolyl Group					
Plane 3: $-0.2195x - 0.8213y - 0.5265z = -7.3267$					
C(17)	−0.019	C(18)	0.020	C(19)	0.001
C(20)	0.005	C(21)	−0.003	C(22)	−0.029
C(23)	0.025				

[a] Dihedral angles (deg): plane 1–plane 2, 7.37; plane 1–plane 3, 87.05; plane 2–plane 3, 85.65.

Table V. Conformational Data for Some Mononuclear Complexes with the Salicylaldiminato Group

compd	dihedral angle,[g] deg	compd	dihedral angle,[g] deg
[Cu(salanil)$_2$][a]	64.9	*N*-salicylidene-3-aminopyridine[e]	14
[Pd(dmba)(salanil)][b]	35.8	*N*-salicylidene-2-aminopyridine[f]	5
[Ir(sal-*o*-tol)(cod)][c]	85.65		
2-chloro-*N*-salicylideneaniline[d]	51		

[a] Reference 18. [b] Reference 9a (dmba = *N*,*N*-dimethylbenzylamine-2-*C*,*N*). [c] This work. [d] Reference 16. [e] Reference 19. [f] Reference 20. [g] Angle between the phenyl substituted group and the salicylaldiminato residue.

nitrogen atom is a phenyl group. Inspection of Table V shows that the iridium compound is the first to be reported in which the *o*-tolyl moiety is almost perpendicular to the remainder of the Schiff base.

^{13}C NMR T_1 Spin-Lattice Relaxation Time Studies

The structural determination shows that, in the solid state, the *o*-tolyl group is roughly perpendicular (Table IV) to the M(1)–M(2)–Ir–O–N plane because of steric hindrances. The molecule has no symmetry element, and thus the atoms of the cyclooctadiene moiety (CH$_2$, =C—H and =C—**H**) are nonequivalent.

In the case of ^{1}H NMR we get precise information only from =C—**H** signals, because the CH$_2$ part of the spectrum is too complicated. The four olefinic protons give three signals at 60 MHz, but they can be resolved into four signals at 350 MHz. We have previously shown high-field signals to correspond to trans-oxygen olefinic protons.[3] This is supported by the fact that for these signals we obtain the largest splitting as they are closer to the source of asymmetry.

The nonequivalence of cod atoms is very clear on the ^{13}C NMR spectra. Even the CH$_2$ atoms give split signals (but only for those closest to the *o*-tolyl group) (Figure 2).

If we considered the spectra of complexes containing the *m*-tolyl group instead of *o*-tolyl, we were unable to find any evidence of nonequivalence for =C—**H** [^{1}H NMR (350 MHz)] or =C—H or CH$_2$ (^{13}C NMR).

To test the hypothesis of a restoration of the equivalence through rotation of the tolyl group, we have undertaken a study of the dynamic properties of [Ir(salanil)(cod)], [Ir(sal-*o*-tol)(cod)], [Ir(sal-*m*-tol)(cod)], and [Ir(salabp)(cod)], using T_1 spin–lattice relaxation time measurements in ^{13}C NMR spectroscopy.

Relaxation of ^{13}C nuclei has been shown to be mainly accomplished through a dipole–dipole and spin rotation mechanism. In our case we established through nuclear Overhauser effect measurements that the only noticeable mechanism for the tertiary and secondary carbon atoms is a dipole–dipole interaction between the C nucleus and the C-bonded H atom. The relaxation rate is then given by

$$R_1 = 1/T_1 = N\gamma_{^{13}\mathrm{C}}{}^2\gamma_{^1\mathrm{H}}{}^2\hbar^2 r_{\mathrm{C-H}}{}^{-6}\tau_{\mathrm{eff}}$$

(where N is the number of protons directly bonded to the carbon atom, $r_{\mathrm{C-H}}$ the carbon–hydrogen distance, and τ_{eff} the effective correlation time for the reorientation of each C–H

Table VI. Relaxation Time (T_1)[a] Measurement Data

	[Ir(salanil)(cod)]	[Ir(sal-*o*-tol)(cod)]	[Ir(sal-*m*-tol)(cod)]	[Ir(salabp)(cod)]
		Cyclooctadiene		
C(1), C(2)	0.80	0.71	0.66	0.56
C(5), C(6)	0.86	0.73	0.70	0.61
C(3), C(8)	0.65	0.60	0.54	0.56
C(4), C(7)	0.59	0.55	0.55	0.55
		Schiff Base		
C(11)	0.81	0.66	0.67	0.72
C(12)	0.83	0.70	0.65	0.50
C(13)	0.87	0.80	0.72	0.62
C(14)	0.89	0.82	0.73	0.67
C(16)	0.94	0.80	0.75	0.64
C(18)	0.92	0.85	0.76	0.67
C(19)	0.98	0.85	0.80	1[g]
C(20)	0.81	0.71	0.66	
C(21)	0.98	0.84		1[g]
C(22)	0.92		0.81	0.67
methyl on C(22)		3.4		
methyl on C(21)			4.8	
phenyl on C(20)				
C(*o*)				1[g]
C(*m*)				1.7
C(*p*)				0.54
average values for C–H	0.88	0.77	0.72	0.77[h]
ρ	1.17[b]	1.19[c]	1.20[d]	1.24,[e] 3.1[f]

[a] T_1 values are in seconds. [b] $\rho = [T_1(\mathrm{C}(18)) + T_1(\mathrm{C}(19))]/2T_1(\mathrm{C}(20))$. [c] $\rho = [T_1(\mathrm{C}(18)) + T_1(\mathrm{C}(19)) + T_1(\mathrm{C}(21))]/3T_1(\mathrm{C}(20))$. [d] $\rho = [T_1(\mathrm{C}(18) + T_1(\mathrm{C}(19)) + T_1(\mathrm{C}(22))]/3T_1(\mathrm{C}(20))$. [e] $\rho = T_1(\mathrm{C}(18))/T_1(\mathrm{C}(p))$. [f] $\rho = T_1(\mathrm{C}(m))/T_1(\mathrm{C}(p))$. [g] The signals corresponding to these atoms are coincident. [h] Value obtained without the coincident signals.

vector). If the motion of the molecule is that of an isotropic rotor, we should have the same value of $N \times T_1$ for each carbon atom, but this is not strictly the case. Discrepancies may be attributed to anisotropy of the overall motion for the rigid part of the molecule and/or to internal motion of the tolyl or phenyl group (Table VI). Differences in absolute values of mean T_1 between the three complexes are related to differences in solubility.

Nevertheless, rotation of the phenyl or tolyl group about the C–N bond should decrease τ_{eff} for the off-axis carbon atoms relative to the value for the tertiary carbon atoms situated on the rotation axis as can be seen by comparing their relaxation time ratios ρ (Table VI).

If we postulate that, in solution, rotation is rigorously prevented for [Ir(sal-*o*-tol)(cod)] then the same would be true for [Ir(salanil)(cod)], [Ir(sal-*m*-tol)(cod)], and the N-bonded phenyl ring in [Ir(salabp)(cod)] for which we have similar ρ values. For this latter compound, however, the free rotation of the terminal phenyl is clearly demonstrated by a significantly greater ρ value. We cannot exclude a limited libration motion of the tolyl or phenyl group around the C–N axis in these compounds, but we can reject the hypothesis of a rapid rotation as a cause of the equivalence of the carbon atoms of the cyclooctadiene in[Ir(sal-*m*-tol)(cod)]. Perhaps the methyl group in the meta position is not sufficient to destroy the local symmetry of these atoms.

The long T_1 values measured for methyl groups indicates in each case a very fast reorientation around their axes.

Acknowledgment. The authors wish to thank Professor R. Chevalier for providing facility for X-ray measurements.

Registry No. 1, R = H, 32761-45-8; **1**, R = 2-CH_3, 68868-44-0; **1**, R = 3-CH_3, 77662-13-6; **1**, R = 4-C_6H_5, 77662-14-7; [Ir(OCH_3)(cod)]$_2$, 33087-83-1.

Supplementary Material Available: Listings of root-mean-square amplitudes of vibration and structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Tetraamidodichromium(II) Compounds and Their Dihalomethane Adducts. Structures of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 1.5C_6H_5CH_3$ and $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Br_2$, M = Cr, Mo

SUBHASH BARAL, F. ALBERT COTTON,* and WILLIAM H. ILSLEY

Received September 11, 1980

The structures of the compounds $Cr_2[(2,6\text{-xylyl})NC(CH_3)O_4] \cdot 1.5C_6H_5CH_3$ (**1**) and $M_2[(2,6\text{-xylyl})NC(CH_3)O]_4 \cdot 2CH_2Br_2$, M = Cr (**2**) and Mo (**3**), are reported. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ and has crystallographic parameters a = 16.219 (2) Å, b = 15.290 (2) Å, c = 19.360 (2) Å, β = 92.21 (1)°, V = 4798 (2) Å^3, and Z = 4. The Cr–Cr bond length is 1.937 (2) Å, and the average Cr–O and Cr–N distances are 1.957 (5) and 2.078 (9) Å, respectively. Associated with each molecule are 1.5 $C_6H_5CH_3$ molecules, one of which occupies a general position within the cell and the other is disordered on an inversion center. Compounds **2** and **3** crystallize in the orthorhombic space group *Pccn* with eight molecules per unit cell. The unit cell constants for the Cr and Mo compounds, respectively, are a = 31.107 (5), 31.300 (4) Å, b = 15.852 (2), 15.944 (3) Å, c = 18.321 (3), 18.378 (2) Å, V = 9034 (4), 9171 (4) Å^3, and Z = 8. Each molecule resides on a general position within the unit cell. The Cr–Cr and Mo–Mo distances are 1.961 (4) and 2.085 (2) Å, respectively. The average M–O and M–N distances are 1.97 (1) and 2.08 (1) Å, and 2.12 (1) and 2.20 (2) Å for the Cr and Mo compounds, respectively. The two CH_2Br_2 moieties occupy positions along the axial extensions of the M–M bonds with M–Br distances of 3.554 (5) and 3.335 (4) Å for the Cr compound and 3.544 (4) and 3.390 (3) Å for the molybdenum compound. The Cr–Cr bond distance in **1** requires revision of our earlier conclusions concerning the extent of axial interactions in **2** and its previously described CH_2Cl_2 analogue.

Introduction

The effect of axial coordination on the metal–metal bond length in quadruply bonded dichromium(II) compounds has been a subject of investigation in our laboratory for the past few years.[1-3] Unlike the dimolybdenum(II) analogues, the quadruply bonded dichromium(II) compounds are unusually good electron-pair acceptors and form bis-axial adducts very easily even with relatively weak Lewis bases, unless the approach of such donor molecules toward the axial site is sterically prohibited. Another interesting difference which makes the chromium compounds unique is the sensitivity of the chromium–chromium quadruple bond length toward the extent of such axial coordination.[1,3] The precise reasons for this qualitative difference in behavior of the Cr–Cr and Mo–Mo quadruple bonds is still under study, but the different energies of the M–M σ and σ^* orbitals[4] as well as the very shallow potential energy curve[5] for $Cr_2(O_2CH)_4$ are probably key factors.

We recently reported an example of what was believed to be significant axial donation from a chlorine atom in CH_2Cl_2 to a chromium atom of $Cr_2[(2,6\text{-xylyl})NC(CH_3)O]_4$.[2] In the crystal a CH_2Cl_2 molecule was found at each axial position of the dichromium molecule, with Cl···Cr distances of 3.354 (3) and 3.58 (1) Å. Although even the shorter of these two contacts would not in itself have constituted sufficient evidence for postulating a Cl→Cr donor bond, the additional observation of a Cr–Cr distance equal to 1.949 (2) Å was also invoked. It was noted that this is considerably greater than

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