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Chromium Carbonyl Complexes of Transition Metal Schiff Bases

ZAHIR U. SIDDIQUI

Department of Chemistry, University of Karachi, Karachi-32, Pakistan

and NIALL J. GOGAN

Department of Chemistry, Memorial University of Newfoundland, St. John's, Nfld., A1B 3X7, Canada

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Abstract

The reaction of Cr(II), Co(II), Co(III), Ni(II), Cu(II) and Zn(II) chelates of Schiff bases derived from salicylaldehyde produces mainly derivatives in which a $Cr(CO)_3$ group or groups are π-bonded to a benzene ring. In the *N*-methyl-salicylaldiminato M–$Cr(CO)_3$ complexes the values of the carbonyl stretching vibrations in the IR increase with the number of d-electrons in the chelated metal indicating that the principal effect is σ-donation from the chelated metal to the $Cr(CO)_3$ group. The *N,N'*-ethylenebis(salicylideneiminato) M–$Cr(CO)_3$ complexes show a similar effect. The *N*-phenyl-salicylaldiminato M–$Cr(CO)_3$ complexes however do not show any trend of carbonyl stretching values with numbers of d-electrons. In addition to the $Cr(CO)_3$ complexes, Zn(II) bis(*N*-methyl-salicylaldiminato) forms a complex in which a $Cr(CO)_4$ group with local C_{4v} symmetry is σ-coordinated to the oxygen atoms of the Schiff base.

Introduction

Complexes containing two metal atoms bonded to different parts of a conjugated molecule are of interest because of the potential for electron delocalization between the metal atoms via the ligand system. Most series of such complexes reported to date have the two metal atoms π-bonded to the ligand such as in the $(CO)_3Cr$ aroylcyclopentadienyl $Mn(CO)_3$ series [1]. An earlier study by us on $(CO)_3Cr$ tetraphenylporphinmetals have shown one π-bonded and one σ-bonded metal [2]. Tricarbonylchromium complexes of metal Schiff bases derived from salicylaldehyde provide an opportunity of studying a series of complexes where the benzene ring is an integral part of the conjugated system rather than on the periphery as in the metal tetraphenylporphin series. In addition, the reaction of such metal Schiff bases with $Cr(CO)_6$ provides the opportunity for the preparation of a σ-bonded tetracarbonylmetal complex of a metal Schiff base of which there have been very few examples reported.

The reaction of *N,N'*-ethylenebis(salicylideneiminato)nickel(II) [Ni(II)(salen)] with $M(CO)_6$ (M = M or W) was reported by Hobday and Smith [3] to yield Ni(II)(salen)$M(CO)_4$ in which the Mo or W atom is σ-bonded to the oxygen atoms of the salen skeleton. No other examples of such complexes are known although Kraihanzel *et al.* synthesized an interesting derivative of a Ni(II) Schiff base containing a $Mo(CO)_4$ group σ-bonded to P atoms at the end of a 'fly-over' chain [4].

Uncomplexed Schiff bases react with Group VI metal hexacarbonyls to yield either metal Schiff bases [5, 6] or σ-coordinated $M(CO)_4$ derivatives [7–13]. It is interesting to note that almost all the latter have the M atom coordinate via N atoms and that the exceptions [10] are S-bonded. No π-bonded $M(CO)_3$ complexes of Schiff bases or metal Schiff bases have been reported.

Experimental

General

UV–Vis spectra ($CHCl_3$) were recorded on a Perkin-Elmer 202 or Unicam SP800 D spectrometer, near IR spectra (nujol mulls) on a Beckman DK-2A spectrometer and IR spectra (KBr) on a Perkin-Elmer 457 spectrometer. Elemental analyses were determined by Alfred Bernhardt or Beller Laboratories (C, H and N) and by atomic absorption spectroscopy (Cr and Co). Melting points (capillary) are reported uncorrected.

Preparation of Schiff Base Chelates

The Zn(II), Co(II), Fe(II) and Mn(II) bis(*N*-methyl-salicylaldiminato) [$(CH_3$-N-sal$)_2$] chelates were prepared by the method of Sacconi *et al.* [14]. The Cu(II) and Ni(II) chelates were prepared by Charles' method [15] and the method of Chakravorty and Holm was used to prepare the Co(III) chelate.

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The bis(*N*-phenyl-salicylaldiminato) chelates, M(II)-(C_6H_5-N-sal)$_2$ were prepared by the methods of West [16] [Co(III)], Sacconi *et al.* [17] [Co(II)], Tyson and Adams [18] [Ni(II)], Percy and Thornton [19] [Zn(II) and Cu(II)]. The [salen] chelates were prepared by the methods of Tsumaki [20] [Co(II)], Hall and Moore [21] [Zn(II)] and Dubsky and Sokal [22] [Cu(II) and Ni(II)]. The melting points (m.p.) were the same or close to the literature values.

Reactions of Zn(II)(CH_3-N-sal)$_2$ with Cr(CO)$_6$

Zn(II)(CH_3-N-sal)$_2$ (0.0045 mol) and Cr(CO)$_6$ (0.009 mol) were reacted in di-n-butyl ether for 6 h under nitrogen using a Soxhlet extractor as previously described [1]. The solvent and excess Cr(CO)$_6$ were removed by evaporation and the remaining solid was purified by fractional precipitation using acetone–pet. spirit (60–80). Two of the fractions showed ν_{CO} in the metal carbonyl region.

The first fraction was an air stable hygroscopic yellow substance which when dried showed a broad band at 3200–3600 cm^{-1} as well as two bands in the ν_{CO} region of the IR. It decomposed at about 100 °C. *Anal.* Zn(II)(CH_3-N-sal)$_2$ [Cr(CO)$_3$]$_2$·3H_2O. Found: C, 39.34; H, 3.53; N, 4.60; Cr, 15.20; Calc. for $C_{22}H_{22}O_{11}N_2ZnCr_2$: C, 40.05; H, 3.36; N, 4.25; Cr, 15.76%. Yield 27%.

The second fraction was an air stable hygroscopic orange substance which when dried showed a broad band at 3200–3600 cm^{-1} as well as four bands in the ν_{CO} region of the IR. It also decomposed at about 100 °C. *Anal.* Zn(II)(CH_3-N-sal)$_2$Cr(CO)$_4$·H_2O. Found: C, 46.56; H, 3.46; N, 5.07, Cr, 10.23. Calc. for $C_{20}H_{18}O_7N_2ZnCr$: C, 46.58; H, 3.52; N, 5.43; Cr, 10.08%. Yield 16%.

Reaction of other Schiff Base Chelates with Cr(CO)$_6$

In a similar fashion the other Schiff base chelates mentioned above were reacted with Cr(CO)$_6$ and separated by fractional precipitation using acetone–pet. spirit or chloroform–pet. spirit. All the well defined complexes are listed in Table I together with m.p.s, elemental analyses and % yields. Most of the compounds are hygroscopic and decompose at about 100 °C. The Co(II) and Mn(II) complexes oxidize easily in solution so all the handling of these compounds was done under nitrogen.

The reaction of both Ni(II)(CH_3-N-sal)$_2$ and Ni(II)(C_6H_5-N-sal)$_2$ with Cr(CO)$_6$ yielded the Cr(II) chelates and a nickel mirror.

Results and Discussion

Structure

With the exception of one of the Zn(II) complexes which will be dealt with later in this paper, all the carbonyl containing products resulting from the reactions of metal Schiff bases with Cr(CO)$_6$ show two bands in the carbonyl stretching region of the IR. This is characteristic of a Cr(CO)$_3$ group bonded to a benzene ring. Most of these complexes exhibit a broad band in the 3200–3600 cm^{-1} region of the IR indicative of water of crystallization. The elemental analyses (Table I) of such complexes agree with one or more water molecules being present in the structure. This is consistent with the observation that the complexes are hygroscopic.

Electronic spectra and magnetic susceptibilities have proven to be very useful in determining the stereochemistry around the metal atom in transition metal Schiff base complexes. Octahedral and tetrahedral structures of bis(R-N-sal)Co(II) (R = alkyl or aryl) can be differentiated by magnetic moments [17] higher values (4.8–5.2 BM) being predicted and observed for octahedral and lower values (4.2–4.6 BM) for tetrahedral stereochemistries. The magnetic susceptibility difference between tetrahedral and square planar Co(II) is clear-cut the latter having values of 2.1–2.9 BM. The magnetic moments of the Cr(CO)$_3$ complexes of Co(II) Schiff bases and the stereochemistries inferred from them are included in Table II.

Three d–d transitions are predicted for Co(II) O_h complexes; ${}^3T_{1g}(F) \rightarrow {}^3T_{2g}(\nu_1)$, ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(\nu_2)$ and ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)\nu_3$. The ν_2 transition, being two-electron, is usually not observed and in this case (Table II) was calculated from the values of ν_1 and ν_3 [23]. The agreement between the values and the Tanabe-Sugano plots support the assignment of O_h symmetry for the bis(C_6H_5-N-sal)Co(II)Cr(CO)$_3$ complexes. Similar calculations support the assignment of *Td* symmetry for bis(CH_3-N-sal)Co(II)-Cr(CO)$_3$·2H_2O. The nature of the salen ligand constrains the stereochemistry of Co(II)(salen)-Cr(CO)$_3$·2H_2O to square planar. The observed μ_{eff} and electronic spectra are in agreement with this stereochemistry [24].

The three Cr(CO)$_3$ complexes of Co(III)(R-N-sal) (R = CH_3, C_6H_5) are diamagnetic. Their electronic spectra show a broad shoulder in the 1300–1900 cm^{-1} region. Crystal field theory predicts two spin allowed and two spin forbidden transitions [25], however the intense ligand and charge transfer bands most likely prevent the resolution of the d–d transitions. The parent Co(II)(R-N-sal)$_3$ compounds were shown to have a *trans* structure attributed to steric constraints [26]. In these Cr(CO)$_3$ complexes the crowding is even greater therefore the *trans* structure is most likely retained.

Ni(II)(salen)Cr(CO)$_3$·H_2O is diamagnetic and its near IR spectrum consists of a broad shoulder from 12 000–16 000 cm^{-1}. The nature of the salen ligand makes a planar structure likely and the absence of absorption below 10 000 cm^{-1} supports the assignment of a planar structure around the nickel atom [27].

TABLE 1. Analytical Data

Compound	Colour[a]	Yield (%)	C (%)		H (%)		N (%)		[b]Metal (%)	
			Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Cr(II)(CH$_3$-N-sal)$_2$Cr(CO)$_3$	y–g	8	50.01	49.73	3.53	4.66	6.14	6.44	22.79	22.00
Cr(II)(C$_6$H$_5$-N-sal)$_2$Cr(CO)$_3$·3H$_2$O	g	35	54.89	54.93	4.13	4.35	4.41	4.28	16.39	16.12
Cr(II)(C$_6$H$_5$-N-sal)$_2$[Cr(CO)$_3$]$_2$·4H$_2$O	b–g	5	48.74	49.93	3.58	3.98	3.55	3.88	19.78	19.63
Co(II)(CH$_3$-N-sal)$_2$Cr(CO)$_3$·H$_2$O	g	27	47.42	47.13	3.77	4.78	5.82	5.32	12.24	12.37(Co)
Co(II)(C$_6$H$_5$-N-sal)$_2$Cr(CO)$_3$·3H$_2$O	g	10	54.30	54.50	4.09	4.51	4.37	4.20	9.18	9.15(Co)
Co(II)(C$_6$H$_5$-N-sal)$_2$Cr(CO)$_3$·2H$_2$O	g	5	55.87	55.99	3.88	4.12	4.49	4.56	9.45	8.27(Co)
Co(II)(salen)Cr(CO)$_3$·2H$_2$O	b	53	45.89	46.75	3.65	3.89	5.63	5.65	10.46	10.63
Co(III)(CH$_3$-N-sal)$_3$Cr(CO)$_3$·2H$_2$O	g	22	51.19	51.87	4.46	4.56	6.63	6.83	9.32	9.93(Co)
Co(III)(CH$_3$-N-sal)$_3$[Cr(CO)$_3$]$_2$·3H$_2$O	b	13	45.76	46.10	3.84	4.46	5.34	5.15	7.50	8.37(Co)
Co(III)(C$_6$H$_5$-N-sal)$_3$[Cr(CO)$_3$}$_2$·13H$_2$O	b	7.5	46.84	46.94	4.89	4.19	3.64	3.58	5.11	5.45
Ni(II)(salen)Cr(CO)$_3$·H$_2$O	r	9	47.64	47.93	3.37	3.56	5.85	5.86	10.85	10.71
Cu(II)(CH$_3$-N-sal)$_2$Cr(CO)$_3$	b	31	48.78	48.46	3.45	4.74	5.99	6.10	11.11	11.03
Cu(II)(C$_6$H$_5$-N-sal)$_2$Cr(CO)$_3$·5H$_2$O	g	22	51.07	51.07	4.43	4.22	4.11	3.91	7.62	7.93
Cu(II)(salen)Cr(CO)$_3$·2H$_2$O	b–g	11	45.47	45.38	3.61	4.92	5.58	5.77	10.36	10.52
Zn(II)(CH$_3$-N-sal)$_2${Cr(CO)$_3$}$_2$·3H$_2$O	y	27	40.05	39.34	3.36	3.53	4.25	4.60	15.76	15.2
Zn(II)(CH$_3$-N-sal)$_2$Cr(CO)$_4$·H$_2$O	o	16	46.58	46.56	3.52	3.46	5.43	5.07	10.08	10.23
Zn(II)(C$_6$H$_5$-N-sal)$_2$[Cr(CO)$_3$]$_3$·4H$_2$O	y–b	14	44.82	45.37	3.01	3.79	2.99	2.70	16.63	16.50
Zn(II)(salen)Cr(CO)$_3$·2H$_2$O	y	7	45.30	45.51	3.60	3.67	5.56	5.53	10.32	10.71

[a] y = yellow, g = green, b = brown, r = red, o = orange.

[b] Metal is chromium unless otherwise noted.

TABLE II. Magnetic and Electronic Spectral Data[a]

Compound	Structure	μ_{eff} (BM)	Near IR (cm^{-1})	UV–Vis (cm^{-1})
$Cr(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3$	Td	4.91	14000–20000(sh)	25700(ϵ 10000), 33500(ϵ 18000), 23000(sh), 30500(sh)
$Cr(II)(C_6H_5\text{-}N\text{-}sal)_2Cr(CO)_3 \cdot 3H_2O$	Td	4.90	14000–20000(sh)	25500(ϵ 5330), 33500(ϵ 13090), 23000(sh), 30500(sh)
$Cr(II)(C_6H_5\text{-}N\text{-}sal)_2[Cr(CO)_3]_2 \cdot 4H_2O$	Td	4.88	14000–20000(sh)	25000(ϵ 7860), 33000(ϵ 16600), 23000(sh), 30000(sh)
$Co(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3 \cdot H_2O$	Td	4.43	6650, 16700	26000(ϵ 3863), 33500(ϵ 9200), 24000(sh), 30000(sh)
$Co(II)(C_6H_5\text{-}N\text{-}sal)_2Cr(CO)_3 \cdot 3H_2O$	Oh	4.84	8350, (17840), 20130	25350(ϵ 5690), 33100(ϵ 16810), 23000(sh), 30000(sh)
$Co(II)(C_6H_5\text{-}N\text{-}sal)_2Cr(CO)_3 \cdot 2H_2O$	Oh	4.83	7871, (16750), 18000	24500(7510), 33400(ϵ 20990), 23000(sh), 30500(sh)
$Co(II)(salen)Cr(CO)_3 \cdot 2H_2O$	Pl	2.43	8350, 17300, 21780	25600, 34000, 23200(sh), 31800(sh)
$Co(III)(CH_3\text{-}N\text{-}sal)_3Cr(CO)_3 \cdot 2H_2O$	Oh		13000–19000(sh)	25500(ϵ 8820), 33800(ϵ 15490), 23500(sh), 30500(sh)
$Co(III)(CH_3\text{-}N\text{-}sal)_3[Cr(CO)_3]_2 \cdot 3H_2O$	Oh		13000–19000(sh)	26000(ϵ 7890), 33600(ϵ 15420), 24000(sh), 31000(sh)
$Co(III)(C_6H_5\text{-}N\text{-}sal)_3[Cr(CO)_3]_2 \cdot 13H_2O$	Oh		13000–19000(sh)	25000, 33600, 23500(sh), 31000(sh)
$Ni(II)(salen)Cr(CO)_3 \cdot H_2O$	Pl		12500–16400(sh)	23000, 29300, 33700, 22000(sh), 25900(sh)
$Cu(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_3$	Pl	1.82	14300–18200(sh)	25670(ϵ 1622), 33200(ϵ 4560)
$Cu(II)(C_6H_5\text{-}N\text{-}sal)_2Cr(CO)_3 \cdot 5H_2O$	Td	1.89	6670, 8330, 11780–1670(sh)	15180(ϵ 5710), 33360(ϵ 14410), 22800(sh), 29500(sh)
$Cu(II)(salen)Cr(CO)_3 \cdot 2H_2O$	Pl	1.91	16400–22400(sh)	26000(ϵ 7100), 33700(ϵ 8225), 23500(sh), 31500(sh)
$Zn(II)(CH_3\text{-}N\text{-}sal)_2[Cr(CO)_3]_2 \cdot 3H_2O$	Td			L.S.
$Zn(II)(CH_3\text{-}N\text{-}sal)_2Cr(CO)_4 \cdot H_2O$	Td			23300(ϵ5560), 31300(ϵ 13450), 33500(ϵ 13620), 29000(sh)
$Zn(II)(C_6H_5\text{-}N\text{-}sal)_2[Cr(CO)_3]_3 \cdot 4H_2O$	Td			22300(ϵ 2580), 31600(ϵ 10750), 33700(ϵ 10970), 28500(sh)
$Zn(II)(salen)Cr(CO)_3 \cdot 2H_2O$	Pl			L.S.

[a] Abbreviations: Td = tetrahedral; Oh = octahedral; Pl = planar; sh = shoulder; L.S. = low solubility.

Tetrahedral complexes of Co(II) Schiff bases have been shown by Sacconi and Ciampolini [28] to have higher magnetic moments (1.89–1.93 BM) than square planar complexes (1.83–1.86 BM). In addition, their study revealed that the distorted tetrahedral complexes have three bands between 5000 and 21 000 cm^{-1} whereas square planar complexes have a broad absorption in the 14 000–16 000 cm^{-1} region. Based on these observations, the data on the $Cr(CO)_3$ complexes of Cu(II) Schiff bases (Table II) support a planar structure around Cu(II) for the CH_3-N-sal and salen complexes and a tetrahedral structure around Cu(II) for the C_6H_5-N-sal complex.

All four carbonylchromium complexes of Zn(II) Schiff bases are diamagnetic but NMR spectra could not be obtained because of low solubility. The stereochemistry around the Zn atom cannot be determined from the data available but the R-N-sal complexes are assumed to retain their tetrahedral structure [29] and the salen complex its planar configuration. Tetrahedral stereochemistry is also assigned to the $Cr(CO)_3$ complexes of $Cr(II)(R\text{-}N\text{-}sal)_2$ on the basis of magnetic susceptibilities.

The UV-Vis spectra (Table II) have several absorptions and are complicated because both the metal Schiff base and the arene chromium tricarbonyl parts of the molecules are expected to absorb in this region. Arene chromium tricarbonyls usually have three bands, 30 800–32 000 cm^{-1} (log E 4.0–4.3), 36 000–40 000 cm^{-1} (log E 3.7–4.0) and 43 500–47 000 cm^{-1} (log E 4.3–4.8) [30, 31]. The metal Schiff bases have an absorption at 24 000–34 000 cm^{-1} (log E 3.9–4.3) and a shoulder at 34 000–37 000 cm^{-1} [17, 28].

The spectra of tricarbonylchromium complexes of metal Schiff bases have, in general, four absorptions; 24 000–26 000 cm^{-1} (log E 3.3–3.8), 29 000–32 000 (broad shoulder), 33 000–34 000 cm^{-1} (log E 3.9–4.3) and 34 000–37 000 cm^{-1} (broad shoulder). These absorptions are consistent with those expected from a combination of metal Schiff base and arene chromium tricarbonyl absorptions.

Infrared Spectra and Electron Distribution

Bis metal chelates of the type $M(II)(CH_3\text{-N-sal})_2$ have only one type of benzene ring site thus these chelates with one $Cr(CO)_3$ group have the unambiguous type of structure shown in Fig. 1. The only such chelate with two $Cr(CO)_3$ groups, $Zn(II)(CH_3\text{-N-sal})_2[Cr(CO)_3]_2 \cdot 3H_2O$, has obviously both benzene rings complexed. $Co(III)(CH_3\text{-N-sal})_3$ forms both the mono and bis-$Cr(CO)_3$ complexes. The metal Schiff base has trans stereochemistry [24] and it is likely that this stereochemistry is retained in the $Cr(CO)_3$ complexes.

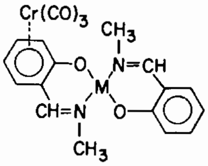

Fig. 1. Structure of the $M(II)(CH_3\text{-N-sal})_2Cr(CO)_3$ complexes.

A plot of ν_{CO} *versus* d^n (Fig. 2) shows that ν_{CO} increases with increasing n and that the relationship is linear except for d^9. If there was significant π-back donation from the chelated metal onto the arene $Cr(CO)_3$ moiety, a decrease in ν_{CO} would be expected as n increases due to the effective decrease in bond order [32]. The observed increase in ν_{CO} with increasing n indicates that the chelated metal is donating σ-electrons onto the CO groups thus increasing the effective C–O bond order.

The interaction of the chelated metal with the ligand can be measured by β, the value of the Racah parameter B for the complex devided by the free ion B value. High values mean a high degree of ionic character and low values a high degree of covalency. The value of β for $Co(II)(CH_3\text{-N-sal})_2Cr(CO)_3 \cdot 2H_2O$, calculated from the near IR data in Table I, is 0.97 indicating almost no covalent character. This would explain the lack of π-back donation observed in the ν_{CO} values. The near IR spectra of the other CH_3-N-sal complexes were not sufficiently resolved to allow the calculation of β.

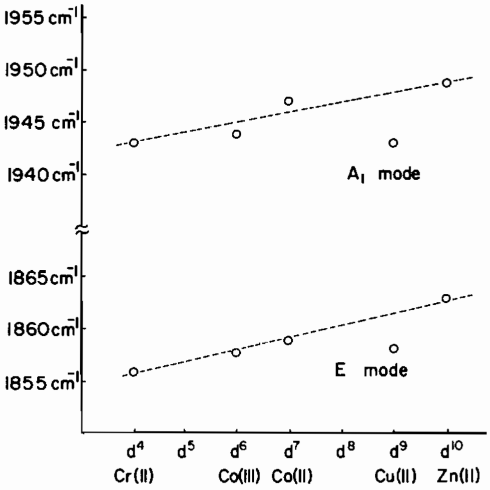

Fig. 2. ν_{CO} *vs.* d^n for $Cr(CO)_3$ complexes of CH_3-N-sal chelates.

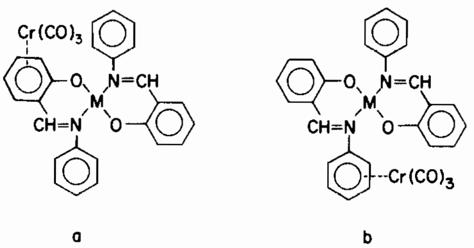

Fig. 3. Possible structures of the $M(II)(C_6H_5\text{-N-sal})_2Cr(CO)_3$ complexes.

In the case of $M(II)(C_6H_5\text{-N-sal})_2$ the $Cr(CO)_3$ groups can be attached to either the disubstituted ring (Fig. 3a) giving a similar structure to the $M(II)(CH_3\text{-N-sal})_2$ complexes or to the monosubstituted ring (Fig. 3b). The ν_{CO} values are substantially higher (7–14 cm^{-1}) in value than for the CH_3 compounds and do not show any trend with d^n [Cr(II) 1956, 1871; Co(III) 1946, 1864; Co(II) 1954, 1874; Cu(II) 1954, 1872 and Zn(II) 1958, 1876 cm^{-1}]. The exception is the Co(III) compound which has ν_{CO} close to that of the CH_3 compound. Because the ν_{CO} values are substantially different than the CH_3 compounds and do not show a trend with d^n, it seems more likely that the $Cr(CO)_3$ groups are attached to the monosubstituted rings (Fig. 3b). NMR spectroscopy of the diamagnetic complexes would most likely have enabled an unambiguous assignment but unfortunately the complexes were too insoluable to obtain spectra. The random nature of the values of ν_{CO} with changing d^n is consistent with complexation of the monosubstituted benzene ring. Unlike the di-

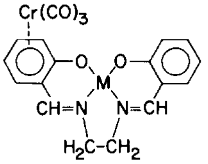

Fig. 4. Structure of the M(II)(salen)$Cr(CO)_3$ complexes.

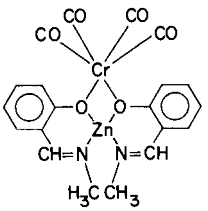

Fig. 5. Structure of the Zn(II)$(CH_3$-N-sal$)_2Cr(CO)_4$ complex.

substituted ring it is free to change its orientation with respect to the metal Schiff base skeleton and hence a change in donation would occur.

The Zn(II)$(C_6H_5$-N-sal$)_2[Cr(CO)_3]_3$ complex must have one of the $Cr(CO)_3$ groups bonded to a different type of benzene ring. It would be expected therefore to show two sets of two bands in the ν_{CO} region. Only two bands are observed but they are broad and could be envelopes containing bands 10 cm^{-1} apart with one of the bands having about half the intensity of the other.

M(II)(salen) forms mono-$Cr(CO)_3$ complexes which have a structure shown in Fig. 4. No Cr(II) or Co(III) complexes were obtained, however a Ni(II) complex, the only one in any of the series, was formed. The lack of a Cr(II) complex considerably limits the range of d^n but the values of ν_{CO} follow the same increasing trend with n[Co(II) 1938, 1849 < Ni(II) 1939, 1852 < Zn(II) 1943, 1858 cm^{-1}] as observed in the CH_3-N-sal series with Cu(II) (1948, 1866 cm^{-1}) again being out of line. This trend strengthens the argument given earlier that the predominent effect is σ-donation from the chelated metal onto the CO groups with no significant π-back donation.

Tetracarbonylchromium Complex

All the chromium carbonyl-containing products from the reactions of Metal Schiff bases with $Cr(CO)_6$ are π-bonded $Cr(CO)_3$ complexes except for one product from the reaction of Zn(II)$(CH_3$-N-sal$)_2$. This stable orange compound has an elemental analysis in agreement with the formula Zn(II)$(CH_3$-N-sal$)_2$-$Cr(CO)_4 \cdot H_2O$ (Fig. 5). It has four ν_{CO} bands at 1948, 1876, 1860 and 1824 cm^{-1}. This is the expected pattern for a σ-bonded $Cr(CO)_4$ group with local C_{4v} symmetry and all the bands are in the usual region for terminal CO. This spectrum is similar to many Schiff base $Cr(CO)_4$ complexes such as *N*,*N*′-ethylenebis-(benzalideneimine) $Cr(CO)_4$ [12]. The bands for Zn(II)$(CH_3$-N-sal$)_2Cr(CO)_4 \cdot H_2O$ are somewhat lower as expected for a $Cr(CO)_4$ group bonded to the more electronegative oxygen atoms as these donate more electrons than nitrogen into the CO antibonding orbitals [32]. The only other similar complexes were reported by Hobday and Smith [3] for Ni(II)(salen). These Mo and W complexes were reported to have four ν_{CO} bands but two of these bands were extremely low (down to 1620 cm^{-1}) for terminal CO and are in the range normally associated with C=O. In our study the reaction of Ni(II)(salen) produced only a $Cr(CO)_3$ π-bonded complex and no $Cr(CO)_4$ derivative.

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