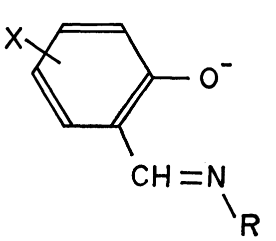
The Effect of Steric Condition in Cobalt(II), Nickel(II) and Copper(II) Complexes with Schiff Bases Obtained from Salicylaldehyde Derivatives and Diphenylmethylamine

Kuniko YAMANOUCHI and Shoichiro YAMADA
Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

(Received September 26, 1975)

Cobalt(II), nickel(II) and copper(II) complexes with *N*-diphenylmethyl-ring-substituted salicylideneiminates (abbreviated as X–Sal–Dpm) have been synthesized, in order to examine the steric and electronic effect of a substituent diphenylmethyl group on the structure of the metal complexes. Compounds of the type $M(X\text{–Sal–Dpm})_2$ and their adducts of the type $M(X\text{–Sal–Dpm})_2 \cdot nL$ have been isolated in crystals, n being 2 or 4 and L being benzene, acetone or pyridine. Both in the solid state and in non-donor solvents, the complexes $Co(X\text{–Sal–Dpm})_2$ have a tetrahedral configuration, and $Ni(X\text{–Sal–Dpm})_2$ and $Cu(X\text{–Sal–Dpm})_2$ have a square-planar configuration, irrespectively of substituents X. The results so far available seem to indicate that the steric hindrance caused by the substituent diphenylmethyl group against the square-planar configuration of the metal complexes may be smaller than that by isopropyl group.

Numerous studies have so far been carried out on 3d transition metal complexes with *N*-substituted salicylideneiminates, which are abbreviated as X–Sal–R (I) in the present paper. These studies have shown that metal complexes of the type $M(X\text{–Sal–R})_2$ vary widely in the structure, depending upon the steric condition arising from R and also upon the electronic effect caused by R on the nitrogen atom.[1–3] For instance, the structure of $M(X\text{–Sal–}n\text{-alkyl})_2$ often differs from that of the complexes with α-branched alkyl for R, mainly because the steric hindrance arising from the α-branched alkyl is remarkably larger than that from *n*-alkyl. The 3d transition metal complexes with *N*-isopropylsalicylideneiminate and its derivatives have been studied, in comparison with the corresponding *n*-alkyl complexes.[4–6] Since diphenylmethyl, abbreviated as Dpm, is related to isopropyl, bearing two phenyl groups instead of two methyl groups in isopropyl, it is thought to be interesting to investigate metal complexes with Schiff bases having diphenylmethyl for R and compare the steric and electronic effects of the substituent Dpm upon the structure of their metal complexes with those of α-branched alkyls.



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In the present work, cobalt(II), nickel(II) and copper(II) complexes with *N*-diphenylmethyl-ring-substituted salicylideneiminates have been synthesized and their structures examined mainly on the basis of their electronic absorption spectra and magnetic data.

Experimental

Materials. Analytical data of new complexes prepared in the present work are shown in Tables 1 and 2.

Bis(N-*diphenylmethylsalicylideneiminato*)*copper*(*II*), *Cu*(*H–Sal–Dpm*)$_2$. Diphenylmethylamine (0.01 mol) was added to a suspension of bis(salicylaldehydato)copper(II) (0.01 mol) in ethanol (50 ml) at about 60 °C and heated with stirring at this temperature for about 30 min. A brown precipitate was recrystallized from chloroform to yield olive-green crystals.

Bis(N-*diphenylmethyl-5-chlorosalicylideneiminato*)*copper*(*II*), *Bis*(N-*diphenylmethyl-5-bromosalicylideneiminato*)*copper*(*II*) and *Bis*(N-*diphenylmethyl-3-methoxysalicylideneiminato*)*copper*(*II*) were prepared as crystals by a method similar to that described above. These copper(II) complexes are olive-green (X=5-Cl, 5-Br) or brown ($X=3\text{-}CH_3O$). They are highly soluble in chloroform and benzene, moderately soluble in acetone and pyridine, and sparingly soluble in methanol and ethanol.

Bis(N-*diphenylmethyl-5-chlorosalicylideneiminato*)*copper*(*II*) *Bis*(*pyridine*)-*adduct*, *Cu*(*5-Cl–Sal–Dpm*)$_2$·*2py*. The parent complex was dissolved in pyridine at 50—60 °C, filtered while the solution was hot, and allowed to stand overnight in a refrigerator. Green crystals of the bis(pyridine)-adduct were collected by filtration.

Bis(N-*diphenylmethyl-5-bromosalicylideneiminato*)*copper*(*II*) *Tetrakis*(*pyridine*)-*adduct*, *Cu*(*5-Br–Sal–Dpm*)$_2$·*4py*. A similar procedure to that described above yielded green crystals of the tetrakis(pyridine)-adduct.

Bis(pyridine)-adduct of the same parent complex was isolated, when recrystallization was carried out from pyridine–ethanol (2:1) or pyridine–chloroform (2:1) mixture instead of pyridine itself.

Both these adducts readily lose pyridine molecules, when left in the atmosphere.

Bis(N-*diphenylmethyl-ring-substituted salicylideneiminato*)*nickel*(*II*), *Ni*(*X–Sal–Dpm*)$_2$ (*X=H, 5-Cl, 5-Br, 3-CH$_3$O*). Complexes of this type were prepared by a method similar to that for the copper(II) complexes. They are olive-green (X=H, 5-Cl, 5-Br) or greenish brown ($X=3\text{-}CH_3O$). They are highly soluble in chloroform and benzene, moderately soluble in acetone and hot pyridine, and sparingly soluble in methanol, ethanol and cold pyridine.

Bis(N-*diphenylmethyl-3-methoxysalicylideneiminato*)*nickel*(*II*) *Tetrakis*(*pyridine*)-*adduct*, *Ni*(*3-CH$_3$O–Sal–Dpm*)$_2$·*4py*. was obtained in green crystals, when the parent complex was recrystallized from pyridine. Bis(pyridine)-adduct could not be isolated by procedures similar to those described above.

All these pyridine adducts of the nickel(II) complexes are much more stable in the atmosphere than the corresponding adducts of the copper(II) and cobalt(II) complexes. They are soluble in benzene, chloroform and acetone, but only

TABLE 1. ANALYTICAL DATA OF COMPLEXES OF THE TYPE M(X–Sal–Dpm)$_2$ AND RELATED COMPOUNDS

Compound	Calcd, %			Found, %			μ
	C	H	N	C	H	N	
Cu(H–Sal–Dpm)$_2$	75.51	5.07	4.40	74.75	5.06	4.45	1.9
Cu(5-Br–Sal–Dpm)$_2$	60.50	3.81	3.53	60.94	4.01	3.50	1.9
Cu(5-Cl–Sal–DPM)$_2$	69.55	4.29	3.97	69.33	4.28	4.01	1.9
Cu(3-CH$_3$O–Sal–Dpm)$_2$	72.46	5.21	4.02	72.51	5.23	4.03	2.0
Ni(H–Sal–Dpm)$_2$	76.09	5.11	4.44	75.92	5.20	4.56	dia
Ni(5-Br–Sal–Dpm)$_2$	60.87	3.83	3.55	60.23	3.78	3.44	dia
Ni(5-Cl–Sal–Dpm)$_2$	68.63	4.32	4.00	68.73	4.32	3.89	dia
Ni(3-CH$_3$O–Sal–Dpm)$_2$	72.95	5.25	4.05	72.77	5.18	3.98	dia
Co(H–Sal–Dpm)$_2$	76.06	5.11	4.44	76.24	5.08	4.48	4.5
Co(5-Br–Sal–Dpm)$_2$	60.85	3.83	3.55	60.82	3.85	3.56	4.2
Co(5-Cl–Sal–Dpm)$_2$	68.58	4.32	4.00	68.52	4.49	4.04	4.4
Co(5-Br–Sal–Dpm)$_2$·2bz	68.53	5.37	3.56	68.08	5.12	3.47	4.5
Co(5-Br–Sal–Dpm)$_2$·2ac	60.85	3.83	3.55	60.82	3.85	3.56	4.6
Co(5-Cl–Sal–Dpm)$_2$·2bz	72.90	4.94	3.27	71.49	5.05	3.17	4.2
Co(5-Cl–Sal–Dpm)$_2$·2ac	61.01	4.68	3.09	61.10	4.64	3.08	4.2

μ: BM, at room temperature dia: diamagnetic bz: benzene ac: acetone

TABLE 2. ANALYTICAL DATA OF ADDUCTS WITH PYRIDINE

Compound	Calcd, %			Found, %			μ
	C	H	N	C	H	N	
Cu(5-Br–Sal–Dpm)$_2$·2py	63.06	4.23	5.88	63.13	4.17	5.94	
Cu(5-Br–Sal–Dpm)$_2$·4py	64.89	4.54	7.57	64.29	4.54	7.42	
Cu(5-Cl–Sal–Dpm)$_2$·2py	69.56	4.67	6.49	69.68	4.64	6.42	2.0
Ni(H–Sal–Dpm)$_2$·2py	76.06	5.36	7.10	75.89	5.46	7.22	3.0
Ni(5-Br–Sal–Dpm)$_2$·2py	63.39	4.26	5.91	63.15	4.25	5.89	3.2
Ni(5-Br–Sal–Dpm)$_2$·4py	65.18	4.56	7.60	65.57	4.58	7.83	2.9
Ni(5-Cl–Sal–Dpm)$_2$·2py	69.93	4.70	6.52	70.56	4.78	6.87	3.1
Ni(3-CH$_3$O–Sal–Dpm)$_2$·4py	73.88	5.60	8.34	74.35	5.65	8.34	3.0
Co(H–Sal–Dpm)$_2$·2py	76.03	5.36	7.09	75.88	5.51	7.29	4.8
Co(5-Br–Sal–Dpm)$_2$·2py	63.37	4.25	5.91	63.12	4.42	5.88	4.9
Co(5-Br–Sal–Dpm)$_2$·4py	65.16	4.56	7.60	65.85	4.62	7.65	4.8
Co(5-Cl–Sal–Dpm)$_2$·2py	69.56	4.67	6.49	69.68	4.64	6.42	5.0
Co(3-CH$_3$O–Sal–Dpm)$_2$·4py	73.87	5.60	8.34	73.72	5.67	8.01	5.0
Co(5-Br–Sal–*i*-pr)$_2$·2py	51.52	4.61	8.01	51.38	4.68	8.11	4.9
Co(5-NO$_2$–Sal–*i*-pr)$_2$·2py	57.05	5.11	13.30	57.33	5.16	13.37	4.8
Co(5-NO$_2$–Sal–Ch)$_2$·2py	60.75	5.67	11.81	61.14	5.60	12.01	4.9
Co(3-CH$_3$O–Sal–Ch)$_2$·2py	66.95	6.80	8.22	66.87	6.75	8.16	4.9

μ: BM, at room temperature py: pyridine pr: propyl Ch: cyclohexyl

slightly soluble in methanol, ethanol and cold pyridine.

Bis(N-*diphenylmethylsalicylideneiminato*)*cobalt*(*II*), *Co*(*H–Sal–Dpm*)$_2$. This complex was synthesized in the same way as the corresponding copper(II) complex. Recrystallization of the crude product from benzene or chloroform yielded red-orange crystals of the pure complex.

Bis(N-*diphenylmethyl-5-halogenosalicylideneiminato*)*cobalt* (*II*), *Co*(*X–Sal–Dpm*)$_2$ (*X*=*5-Cl*, *5-Br*). The crude products of these complexes were prepared in the same way as described above for Co(H–Sal–Dpm)$_2$. It was not possible to find a suitable solvent for recrystallization. Attempts to recrystallize them yielded either products of insignificant composition or adducts with solvents used in the recrystallization, instead of the pure parent complex.

The pure complexes of the type Co(X–Sal–Dpm)$_2$ were obtained by heating bis(benzene)- or bis(acetone)-adduct (*vide infra*) for about 4 hr at about 80 °C under reduced pressure.

These cobalt(II) complexes are soluble in chloroform, benzene and acetone, but sparingly soluble in methanol, ethanol and cold pyridine.

Bis(N-*diphenylmethyl-5-halogenosalicylideneiminato*)*cobalt*(*II*) *Bis*(*benzene*)- *and Bis*(*acetone*)-*adducts*, *Co*(*X–Sal–Dpm*)$_2$·*2L* (*X*=*5-Cl*, *5-Br*; *L*=*benzene*, *acetone*). Crude products of the parent complexes, which were prepared as described above, were recrystallized from benzene or acetone to yield red-orange crystals of the bis(benzene)- or bis(acetone)-adducts.

Bis(N-*diphenylmethyl-ring-substituted salicylideneiminato*)*cobalt*(*II*) *Bis*(*pyridine*)-*adducts*, *Co*(*X–Sal–Dpm*)$_2$·*2py* (*X*=*H*, *5-Cl*). Compounds of this type were isolated in yellow-orange crystals by a method similar to that for the corresponding nickel(II) compounds.

Bis(N-*diphenylmethyl-5-bromosalicylideneiminato*)*cobalt* (*II*) *Tetrakis*(*pyridine*)- *and Bis*(*pyridine*)-*adducts*, *Co*(*5-Br–Sal–Dpm*)$_2$·n*py* (n=2,4) were isolated in yellow-orange crystals by a method similar to that for the corresponding nickel(II) compounds.

Bis(N-*diphenylmethyl-3-methoxysalicylideneiminato*)*cobalt* (*II*)

Tetrakis(pyridine)-adduct, Co(3-CH$_3$O-Sal-Dpm)$_2$·4py, was obtained in yellow-orange crystals in the same way as described above for the corresponding nickel(II) complex. It has not been possible so far to isolate crystals of the parent complex, Co(3-CH$_3$O–Sal–Dpm)$_2$.

All these pyridine adducts of the cobalt(II) complexes lose pyridine molecules comparatively slowly, when left in the atmosphere. They are considerably soluble in benzene, chloroform and acetone, but only slightly soluble in methanol, ethanol and cold pyridine.

With the cobalt(II), nickel(II) and copper(II) complexes, only bis- and/or tetrakis(pyridine)-adducts were obtained, and adducts of another type, such as mono- and tris-(pyridine)-adducts, have not been isolated.

Bis(N-*isopropyl-ring-substituted salicylideneiminato*)*cobalt*(*II*) *Bis*(*pyridine*)-*adducts, Co*(*X–Sal–i-C$_3$H$_7$*)$_2$·*2py* (*X=5-Br, 5-NO$_2$*), were obtained in yellow-orange crystals by recrystallizing the parent complex from pyridine or by adding *n*-hexane into a hot solution of the parent complex in pyridine.

Bis(N-*cyclohexyl-ring-substituted salicylideneiminato*)*cobalt*(*II*), *Co*(*X-Sal-Ch*)$_2$ (*X=5-Cl, 5-Br, 5-NO$_2$, 3-CH$_3$O*), were prepared, as previously reported, Ch being cyclohexyl.[6]

Bis(N-*cyclohexyl-ring-substituted salicylideneiminato*)*cobalt*(*II*)*bis*(*pyridine*)-*adducts, Co*(*X-Sal-Ch*)$_2$·*2py* (*X=5-NO$_2$, 3-CH$_3$O*) were obtained in yellow-orange crystals by recrystallizing the parent complexes from pyridine or by adding hexane into a hot solution of the parent complexes in pyridine.

Measurements. Electronic absorption spectra of the complexes were measured on a Shimadzu MPS-50L spectrophotometer. Infrared spectra were obtained from Nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer.

Magnetic measurements were carried out by the Gouy method at room temperature using CoHg(SCN)$_4$ as a calibrant.

Since many of the adducts underwent decomposition during the measurements, only those data which may be regarded as accurate and reliable enough for discussion are shown in the tables. Solubility of complexes Co(X–Sal–Dpm)$_2$ and Ni(X–Sal–Dpm)$_2$ in appropriate solvents including pyridine is not high enough for spectral measurements.

Results and Discussion

Cobalt(II) Complexes. When cobalt(II) acetate, salicylaldehyde and diphenylmethylamine are refluxed in the atmosphere in the presence of alkali, such as sodium carbonate, bis(*N*-diphenylmethylsalicylideneiminato)cobalt(II) is readily obtained, oxidation to the cobalt(III) complex hardly being observed. Any attempt to isolate the tris(Schiff base)cobalt(III) complex has not so far been successful even with hydrogen peroxide.

Previous studies have shown that a similar procedure in the atmosphere readily yields the cobalt(III) complexes of the corresponding Schiff bases, when *n*-alkylamines are employed instead of diphenylmethylamine.[2a] A similar procedure using isopropylamine, *t*-butylamine or arylamines yields only bis(Schiff base)-cobalt(II) complex.[6] Tris(*N*-isopropyl-ring-substituted salicylideneiminato)cobalt(III) complexes,[7] as well as tris(*N*-arylsalicylideneiminato)cobalt(III),[8] are obtained by more effective oxidation using hydrogen peroxide.

Comparison seems to indicate that greater difficulty is encountered in obtaining Co(X–Sal–Dpm)$_3$ than Co(X–Sal–*i*-C$_3$H$_7$)$_3$, although it may not be plausible to say definitely that Co(X–Sal–Dpm)$_3$ cannot be isolated at all. The difference in this respect between Dpm and isopropyl may be discussed in terms of the two factors: (a) ligand field strength and (b) steric condition.

It is known that the higher stability of the sexa-coordinated cobalt(III) complex is attained with ligands producing a stronger ligand field. It is expected and has also been confirmed by some experimental results[1,2] that the ligand field of X–Sal–R depends upon the nature of substituents R and decreases in the following order: aryl$<$CH(ph)$_2$$<CH_2ph<$*n*-alkyl$<$*i*-C$_3H_7$, where ph denotes phenyl group. Thus X–Sal–Dpm would produce a slightly weaker ligand field than X–Sal–*i*-C$_3$H$_7$. Therefore, so far as the factor of the ligand field strength is concerned, X–Sal–Dpm would form the tris(Schiff base)-cobalt(III) less readily than X–Sal–*i*-C$_3$H$_7$, in agreement with the experimental results.

Alternatively, in order to explain the observed results, one might argue that larger steric hindrance against formation of the tris(Schiff base)cobalt(III) complex would be created by X–Sal–Dpm than by X–Sal–*i*-C$_3$H$_7$. This explanation, however, may not be adequate, since in fact, the reverse seems to be the case. The truth is that larger steric hindrance may be exercised by X–Sal–*i*-C$_3$H$_7$ than by X–Sal–Dpm in formation of both th square-planar bis(Schiff base)-nickel(II) complexes and the sexa-coordinated bis(pyridine)-adducts of the cobalt(II) complexes, as will be discussed later in this paper. Nevertheless, the steric factor, besides the electronic factor, is also considered to play at least a minor role in preventing the tris-complex formation.

It should be noted that benzene or acetone adducts are obtained, when recrystallization of Co(X–Sal–Dpm)$_2$ is carried out from benzene or acetone, X being Cl and Br. As shown in Table 3, spectra of the benzene adducts are typical of the tetrahedral cobalt(II) complexes. It is presumed that the benzene adducts consist of tetrahedral cobalt(II) complexes and non-coordinated benzene molecules, which presumably occupy interstice in the crystal lattices. The benzene adducts, when dissolved in benzene, show nearly the same electronic spectra as those of the parent complexes, which are typical of the tetrahearal cobalt(II) complexes, as shown in Table 3.

The acetone adducts also show electronic spectra, which are essentially the same as those of the parent complexes. Moreover, the adducts show a strong infrared band at 1700 cm^{-1}, which is assigned to a C=O stretching frequency of a free acetone molecule. It is, therefore, reasonable to consider that they consist of the tetrahedral cobalt(II) complexes and non-coordinated acetone molecules. This conclusion is also supported by the finding that the spectrum of Co(5-Cl–Sal–Dpm)$_2$ in acetone is almost identical with that of the same complex in benzene, showing that the acetone molecule is not bound with the cobalt(II) ion.

It is interesting to note that both bis(pyridine)- and tetrakis(pyridine)-adducts of the cobalt(II) complexes are isolated for X=H, 5-Cl, 5-Br and 3-CH$_3$O. Although they lose pyridine molecules slowly, they are

Table 3. Main d-d absorption maxima of M(X–Sal–Dpm)$_2$ and their benzene and acetone adducts

Compound	Solvent	ν (log ε)
Ni(H–Sal–Dpm)$_2$	CH_2Cl_2	16.5(1.94), 19.5(2.05)sh
Ni(5-Cl–Sal–Dpm)$_2$	CH_2Cl_2	16.4(2.01), 19.3(2.10)sh
Ni(5-Br–Sal–Dpm)$_2$	CH_2Cl_2	16.4(2.00), 19.4(2.10)sh
Ni(3-CH_3O–Sal–Dpm)$_2$	CH_2Cl_2	16.3(2.06), 19.3(2.10)sh
Co(H–Sal–Dpm)$_2$	CH_2Cl_2	8.3(1.79), 10.8(1.50)sh, 18.6(1.80)
Co(5-Br–Sal–Dpm)$_2$	$CHCl_3$	8.1(1.84), 10.5(1.55)sh, 18.1(1.80)sh
Co(5-Cl–Sal–Dpm)$_2$	$CHCl_3$	8.1(1.82), 10.6(1.45)sh, 18.2(1.80)sh
	benzene	8.2(1.81), 10.6(1.60)sh, 18.2(1.90)sh
	acetone	8.2(1.81), 10.5(1.60)sh, 18.3(1.98)sh
Co(5-Cl–Sal–Dpm)$_2$·2bz	Nujol	8.2, 10.5, 18.2
Co(5-Br–Sal–Dpm)$_2$·2ac	Nujol	8.2, 10.5, 18.3

ν: kK

crystalline and their analytical data agree only with either the bis- or tetrakis(pyridine)-adduct. The reason why another type of adduct, for example, mono- or tris-(pyridine)-adduct does not occur is not clear. Both the bis- and tetrakis-(pyridine)-adducts show electronic spectra typical of sexa-coordinated bis(pyridine)bis(*N*-substituted salicylideneiminato)cobalt(II) complexes, as shown in Table 4. The d-d band at about 10 kK may be assigned to a transition $^4T_{2g} \leftarrow {}^4T_{1g}$ in the scheme of the O_h ligand field symmetry. It is, therefore, presumed that they contain sexa-coordinated bis(pyridine)-cobalt(II) complexes, which probably have a *cis*-structure, judging from the steric condition.

Now we may compare the data in the present work with those for complexes of the type Co(X–Sal–*i*-C_3H_7)$_2$. In previous papers,[2] Co(H–Sal–*i*-C_3H_7)$_2$ was reported to have very low capacity to form a sexa-coordinated bis(pyridine)-adduct, which has not been isolated in crystals so far. Even in pyridine, at least 90% of it exists as the original tetrahedral cobalt(II) complex.[6,9] This is in contrast to the behavior of Co(H–Sal–Dpm)$_2$, which readily forms a bis(pyridine)-adduct. The difference in this respect between these two series of cobalt(II) complexes may be ascribed mainly to the steric factor. The steric factor, however, seems to be rather delicate and not the only dominant factor in this case. The effect of the substituent X on the electronic state of the nitrogen atom in the Schiff base may also play a significant part. As shown in Table 4, when dissolved in pyridine, the complexes Co(X–Sal–*i*-C_3H_7)$_2$, X being 5-Cl, 5-Br and 5-NO_2, consist almost entirely of sexa-coordinated bis(pyridine)-adducts, some of which can be isolated in crystals from their pyridine solutions. The bis(pyridine)-adducts have magnetic moments of 4.8 to 5.1 BM and show electronic spectra typical of the sexacoordinated cobalt(II) complex with a d-d band maximum at about 10 kK. The remarkable difference between Co(H–Sal–*i*-C_3H_7)$_2$ and Co(X–Sal–*i*-C_3H_7)$_2$, X being 5-Cl, 5-Br and 5-NO_2, seems to be noteworthy. The effect of the substituent X is found to be significant.

Table 4. Main d-d absorption maxima of M(X–Sal–Dpm)$_2$·*n*py and related compounds

Compound	Solvent	ν (log ε)
Ni(H–Sal–Dpm)$_2$·2py	Nujol	11.0, 17.9
Ni(5-Br–Sal–Dpm)$_2$·2py	Nujol	11.0, 17.9
Ni(5-Br–Sal–Dpm)$_2$·4py	Nujol	11.0, 17.8
Ni(5-Cl–Sal–Dpm)$_2$·2py	Nujol	10.7, 17.8
Ni(3-CH_3O–Sal–Dpm)$_2$·4py	Nujol	10.9, 17.9
Co(H–Sal–Dpm)$_2$·2py	Nujol	10.7, 17.8 sh
Co(5-Br–Sal–Dpm)$_2$·2py	Nujol	10.6, 17.5 sh
Co(5-Br–Sal–Dpm)$_2$·4py	Nujol	10.6, 17.7 sh
Co(5-Cl–Sal–Dpm)$_2$·2py	Nujol	10.6, 17.7 sh
Co(3-CH_3O–Sal–Dpm)$_2$·4py	Nujol	10.7, 17.5 sh
Co(5-Br–Sal–*i*-pr)$_2$	pyridine	10.3 (1.02), 17.8 (1.32) sh
Co(5-Br–Sal–*i*-pr)$_2$·2py	Nujol	10.2, 17.8
Co(5-Cl–Sal–*i*-pr)$_2$	pyridine	10.3 (1.08), 17.9 (1.35) sh
Co(5-NO_2–Sal–*i*-pr)$_2$	pyridine	10.0 (1.12), 17.6 (1.35) sh
Co(5-NO_2–Sal–*i*-pr)$_2$·2py	Nujol	10.1, 17.8 sh
Co(5-Br–Sal–Ch)$_2$	pyridine	10.3 (0.95), 17.7 (1.32) sh
Co(5-Cl–Sal–Ch)$_2$	pyridine	10.1 (1.01), 17.7 (1.33) sh
Co(5-NO_2–Sal–Ch)$_2$	pyridine	10.0 (1.16), 17.8 (1.40) sh
Co(5-NO_2–Sal–Ch)$_2$·2py	Nujol	10.2, 17.6
Co(3-CH_3O–Sal–Ch)$_2$	pyridine	10.2 (1.10), 17.7 (1.35) sh
Co(3-CH_3O–Sal–Ch)$_2$·2py	Nujol	10.2, 17.6

ν: kK pr: propyl Ch: cyclohexyl

Comparison of Co(X-Sal-Dpm)$_2$ with Co(X-Sal-Ch)$_2$, Ch being cyclohexyl group, may also be interesting. Previous studies have shown that in pyridine, nearly 50% of Co(H-Sal-Ch)$_2$ exists as the original tetrahedral cobalt(II) complex.[6,9] However, it has not so far been possible to isolate bis(pyridine)-adduct. Instead, mono-pyridine-adduct was isolated as red crystals.[10] The effect of the substituent X is again found to be remarkable in the cyclohexyl complexes. As shown in Table 4, electronic spectra indicate that the complexes Co(X-Sal-Ch)$_2$ in pyridine, X being 5-Cl, 5-Br, 5-NO$_2$ and 5-CH$_3$O, exist totally as sexa-coordinated bis(pyridine)-adducts. Some of them can also be isolated in crystals from their pyridine solutions, as shown in Table 2. Electronic spectra of these bis(pyridine)-adducts have a d-d band with a maximum at about 10 kK, which is typical of the sexa-coordinated cobalt(II) complex.

Inspection of the data so far available indicates that the relative tendency of Co(X-Sal-R)$_2$ to form sexa-coordinated bis(pyridine)-adducts increases according to the substituent R in the following order: $\mathrm{CH(ph)_2} < \mathrm{Ch} < \mathrm{CH(CH_3)_2} < \mathrm{C(CH_3)_3}$. This order seems to be in agreement with the order for the steric hindrance arising from the substituent.

Nickel(II) and Copper(II) Complexes. As shown in Tables 1 and 3, complexes of the type Ni(X-Sal-Dpm)$_2$ are diamagnetic in the solid state and show electronic absorption spectra typical of the square-planar nickel(II) complex in non-donor solvents. No absorption band is observed at about 10—11 kK or lower frequencies, where the octahedral or tetrahedral nickel(II) complex is expected to absorb. So far, any tetrahedral species has been neither isolated in crystals, nor detected in the solutions at room temperature for nickel(II) complexes of the type Ni(X-Sal-Dpm)$_2$. This result is in contrast to the result previously reported for complexes of the type Ni(X-Sal-*i*-C$_3$H$_7$)$_2$, which exist in non-donor solvents at room temperature in a conformational equilibrium of the planar diamagnetic and pseudo-tetrahedral paramagnetic forms.[4] The equilibrium depends upon the nature of the substituents R; Ni(H-Sal-*i*-C$_3$H$_7$)$_2$ in non-donor solvents at room temperature exists almost totally as the tetrahedral species. Moreover, both tetrahedral and squre-planar species of Ni(X-Sal-*i*-C$_3$H$_7$)$_2$ were previously isolated.[2b,4,5,11] Comparison indicates that the steric hindrance against the square-planar configuration in the complexes Ni(X-Sal-Dpm)$_2$ is smaller than in Ni(X-Sal-*i*-C$_3$H$_7$)$_2$.

Just like the corresponding cobalt(II) complexes, both bis- and tetrakis-(pyridine)-adducts of the nickel(II) complexes are readily isolated. They are of a high spin type and show electronic absorption spectra typical of sexa-coordinated nickel(II) complexes, having a d-d band at about 11 kK, as shown in Table 4. The band at about 11 kK may be assigned to a $^3T_{2g} \leftarrow {}^3A_{2g}$ transition in the scheme of O_h field symmetry. It is presumed, therefore, that they all contain sexa-coordinated bis(pyridine)nickel(II) complexes. A similar trend was previously reported for complexes of the type Ni(X-Sal-*i*-C$_3$H$_7$)$_2$, which form sexa-coordinated bis-(pyridine)-adducts, when dissolved in pyridine.[12]

Electronic absorption spectra of copper(II) complexes of the type Cu(X-Sal-Dpm)$_2$ in non-donor solvents are similar to each other and nearly identical with the spectra of complexes Cu(X-Sal-*n*-alkyl)$_2$, having the first d-d band with a maximum at about 17 kK (log ε 2—2.2) and a shoulder at about 22 kK (log ε 2.8—3.0). It may, therefore, be reasonable to presume that these complexes in non-donor solvents have an essentially square-planar configuration.

It should be noted that the spectra of Cu(H-Sal-Dpm)$_2$ in non-donor solvents are remarkably different from those of Cu(H-Sal-*i*-C$_3$H$_7$)$_2$,[4,5] which was concluded to contain pseudo-tetrahedral species. The latter complex shows the first d-d band with a maximum at about 15.7 kK, which is found to be shifted toward a considerably lower frequency than that of the former (17 kK). The difference between these two complexes also seems to be in agreement with the assumption that the steric hindrance against the square-planar configuration is smaller in the complexes Cu(X-Sal-Dpm)$_2$ than in Cu(X-Sal-*i*-C$_3$H$_7$)$_2$.

Spectra of Cu(X-Sal-Dpm)$_2$ in pyridine differ significantly from their spectra in non-donor solvents; the latter have more broad d-d bands at about 15.5 kK, which is found to be shifted toward lower frequencies, as compared with the corresponding band of the solutions in non-donor solvents. The spectral change in the d-d band region of these copper(II) complexes on going from a non-donor solvent to pyridine is similar to the change observed previously when the quadri-coordinated complex of copper(II) takes up one or two additional pyridine molecules to form a penta- or sexa-coordinated complex.[13]

The pyridine adducts, Cu(X-Sal-Dpm)$_2$·*n*py, *n* being 2 and 4, are isolated in crystals. However, they lose pyridine molecules so readily that it has not been possible to obtain reliable data of electronic absorption spectra and magnetic susceptibilities in most cases. Judging from their behavior in the pyridine solutions, it is most likely that some number of pyridine molecules may be bound with the copper(II) ion. From the experimental data so far available, however, it is difficult to know the exact number of pyridine molecules bound with the copper(II) ion.

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