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Complexing Behaviour of N-Sulphinylaniline: Complexes of Mn(II), Fe(II), Ru(II), Co(I), Rh(I), Ni(0), Pd(0), Pt(0), Cu(I) & Ag(I)

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Reactions of N-sulphinylaniline (NSA) with some transition metal ions and complexes have been studied. The complexes, $[MnCl_2-(NSA)_2]$, $[FeCl_2(PPh_3)(NSA)]$, $[RuCl_2(PPh_3)_2(NSA)_2]$, $[RuCl_2(AsPh_3)_2\text{-}(NSA)_2]$, $[CoH(P(OPh)_3)_2(NSA)]$, $[RhCl(PPh_3)(NSA)_2]$, $[Rh(CO)Cl\text{-}(PPh_3)(NSA)]$, $[Ni(P(OPh)_3)_2\,(NSA)_2]$, $[Pd(PPh_3)_2(NSA)_2]$, $[Pt(PPh_3)_2\text{-}(NSA)_2]$, $[CuCl(PPh_3)_2(NSA)]$ and $[Ag(PPh_3)(NSA)]\,(NO_3)$ have been characterised on the basis of elemental analyses, IR and electronic spectral, magnetic and conductivity measurements. N-Sulphinylaniline acts as monodentate and is bonded through its nitrogen atom. Tentative geometries of the complexes have been proposed.

N-Sulphinyl group besides forming covalent and ionic derivatives, has been known to occur in the form of organic sulphinylamines[1,2]. This class of compounds has a pair of terminal and cumulate unsaturated group which takes part in the addition reactions. This interesting behaviour of N-sulphinylamines renders these as interesting ligands for the formation of complexes with transition metal ions. In this paper, the syntheses and the structural studies of complexes of the N-sulphinylaniline (NSA) with some of the transition metal ions have been reported.

Materials and Methods

All the chemicals used were chemically pure or of analar grade. All the solvents were distilled and dried before use. The reactions were carried out under pure and dry nitrogen atmosphere.

N-Sulphinylaniline (NSA), dichlorobis (triphenylphosphine)iron(II), dichlorotris(triphenylphosphine)ruthenium(II), trichlorobis(triphenylarsine)methanol ruthenium(III), hydridotetrakis(triphenylphosphate)cobalt(I), monochlorotris(triphenylphosphine) rhodium(I), carbonylchlorobis(triphenylphosphine)rhodium(I), tetrakis(triphenylphosphite)nickel(0), tetrakis(triphenylphosphine)palladium(0), tetrakis(triphenylphosphine)platinum(0), chlorotris(triphenylphosphine)copper(I) and tetrakis(triphenylphosphine)silver(I) nitrate were prepared by reported methods[1,3-12].

(1) *Dichlorobis(N-sulphinylaniline)-manganese(II)*

A solution (10 ml) of $MnCl_2.4H_2O$ (0.8 g, 4 mmol) in ethyl alcohol was slowly added with stirring to a solution of NSA (2.5 ml, ~16 mmol) in ethyl alcohol (10 ml). On stirring the reaction mixture for 1 hr a pale pink solid separated out, which was centrifuged, washed a few times with ethanol and finally with ether. The vacuum-dried sample did not melt upto 300°; yield ~55%).

(2) *Dichloro(triphenylphosphine)-(N-sulphinylaniline)iron(II)*

Dichlorobis(triphenylphosphine)iron(II) (1.2 g, ~2 mmol) was dissolved in benzene (15 ml) by warming and to the resulting clear solution was added a benzene solution (10 ml) of NSA (1.6 ml, ~10 mmol). The reaction mixture was refluxed for about 1 hr and the resulting dark brown solution concentrated to half of its original volume. On the addition of pet. ether (15 ml, 40-60°), a greyish-green solid precipitated out, which was centrifuged, washed with pet. ether, recrystallized twice from benzene-petroleum ether and dried in a vacuum desiccator; m.p. 185-86°; yield ~60%.

(3) *Dichlorobis(triphenylphosphine)bis-(N-sulphinylaniline)ruthenium(II)*

NSA (0.5 ml, ~3 mmol) in chloroform (7 ml) was slowly added to a dark brown solution of $RuCl_2(PPh_3)_3$ (0.5 g, ~0.5 mmol) in chloroform (10 ml) with stirring. A blue complex was immediately precipitated. Stirring was continued for 1 hr more, the blue complex filtered off, washed with pet. ether and repeatedly recrystallised from a chloroform-pet. ether; m.p. 190-92°; yield ~65%.

(4) *Dichlorobis(triphenylarsine)bis-(N-sulphinylaniline)ruthenium(II)*

To a solution (10 ml) of $RuCl_3(AsPh_3)_2.MeOH$ (0.43 g, ~0.5 mmol) in dichloromethane, a solution of NSA (0.5 ml, 3 mmol) in benzene (10 ml) was gradually added. The resulting brown solution was stirred for 2 hr, concentrated to 10 ml, pet. ether (10 ml) added and the brown solid obtained filtered, washed with *n*-pentane and recrystallised from dichloromethane-pet. ether; m.p. 176-77°; yield ~60%.

(5) *Hydridobis(triphenylphosphite)-(N-sulphinylaniline)cobalt(I)*

A solution (15 ml) of hydridotetrakis(triphenylphosphite)cobalt(I) (1.4 g, 1 mmol) in acetonitrile was added with stirring to a benzene solution (10 ml) of NSA (1 ml, ~6 mmol). On stirring the reaction mixture for 1.5 hr, its pale yellow colour was changed to brown. The brown solution was concentrated to about 10 ml under reduced pressure. On adding ether (10 ml) a pale brown precipitate was obtained. It was centrifuged, washed with ether, recrystallised twice from acetonitrile-ether and dried *in vacuo*; m.p. 158-60°; yield ~48%.

(6) *Monochloro(triphenylphosphine)bis-(N-sulphinylaniline)rhodium(I)*

A solution (15 ml) of monochlorotris(triphenylphosphine)rhodium(I) (0.46 g, ~0.5 mmol) in dichloromethane was gradually added to a solution (10 ml) of NSA (0.5 ml, ~3 mmol) in benzene and the reaction mixture refluxed for 2 hr. The resulting solution was concentrated to about 10 ml under reduced pressure. A light brown complex was precipitated by the addition of pet. ether (10 ml). It was centrifuged, repeatedly washed with pet. ether and dried in a vacuum desiccator; m.p. 210-12°; yield ~60%.

(7) *Carbonylchloro(triphenylphosphine)-(N-sulphinylaniline)rhodium(I)*

To a stirred benzene solution (10 ml) of carbonylchlorobis(triphenylphosphine)rhodium(I) (~0.5 mmol), a solution of NSA (0.5 ml, ~3 mmol) in benzene (8 ml) was gradually added. Stirring was continued for 1 hr more and the resulting brown solution concentrated to about 10 ml under reduced pressure. Addition of pet. ether (10 ml, 60-80°) afforded a yellowish brown solid which was centrifuged and washed with pet. ether. The complex was recrystallised by dissolving it in the minimum amount of benzene, followed by addition of pet. ether. The recrystallisation process was repeated several times until a constant melting complex was obtained; m.p. 238-40°; yield ~68%.

(8) *Bis(triphenylphosphite)bis(N-sulphinylaniline)nickel*(0)

A solution of tetrakis(triphenylphosphite)nickel(0) (1.3 g; ~1 mmol) in chloroform (15 ml) was refluxed with a benzene solution (10 ml) of NSA (1 ml, ~6 mmol) for 2 hr. On cooling the resulting red-brown solution, a brown compound settled down which was centrifuged, repeatedly washed with a benzene-pet. ether (1:3) and dried *in vacuo*; m.p. 169-79°; yield ~38%

(9) *Bis(triphenylphosphine)bis(N-sulphinylaniline)palladium*(0)

To a benzene solution of tetrakis(triphenylphosphine)palladium(0) (0.6 g, 0.5 mmol) was gradually added a solution of NSA (0.5 ml, 3 mmol) in benzene with stirring under dry N_2 atmosphere. After stirring for additional 1 hr, the resulting red-orange solution was concentrated to about 10 ml under reduced pressure and ether (15 ml) added to it. An orange coloured solid precipitated out, which was centrifuged, washed with ethanol and ether, recrystallised from benzene-pet. ether (1:3), dried and kept in a vacuum desiccator; m.p. 138-40°; yield ~55%.

(10) *Bis(triphenylphosphine)bis(N-sulphinylaniline)platinum*(0)

The procedure followed to prepare this complex was the same as that given in (9), except that $Pt(PPh_3)_4$ was taken in place of $Pd(PPh_3)_4$. A pale yellow compound was obtained; m.p. 172-73°; yield ~60%.

(11) *Monochlorobis(triphenylphosphine)-(N-sulphinylaniline)copper(I)*

$CuCl(PPh_3)_3$ (1.8 g, ~2 mmol) was dissolved with stirring in dichloromethane (20 ml) and a solution of NSA (2 ml, ~13 mmol) in dichloromethane (10 ml) slowly added to it. The stirring was continued for 1.5 hr more and the resulting brown solution concentrated to about 10 ml. A pale yellow solid was precipitated by the addition of about 10 ml of pet. ether (60-80°) to the concentrated solution. It was centrifuged, washed with *n*-pentane, recrystallised twice from dichloromethane-pet. ether and dried in a vacuum desiccator; m.p. 220-23°; yield ~43%.

(12) *(Triphenylphosphine)(N-sulphinylaniline)-silver(I) nitrate*

$[Ag(PPh_3)_4](NO_3)$ (1.2 g, ~1 mmol) was dissolved in acetonitrile (15 ml) and refluxed with a solution of NSA (0.6 ml, ~5 mmol) in acetonitrile (10 ml) for 1 hr. The colour of the yellow solution slowly changed to red-brown. On slow cooling, and leaving it for 2-3 hr, a grey coloured compound settled down. It was centrifuged, washed with ether and recrystallised twice from acetonitrile-ether; m.p. > 300°; yield ~38%.

Physical measurements

Infrared spectra of the ligand and the metal complexes were recorded in KBr matrix on a Perkin-Elmer 580 diffraction grating spectrophotometer in the range 4000-250 cm^{-1}. The electronic absorption

Table 1—Analytical Data and Geometries of Complexes

Complexes	Found (%) (Calc.)						Geometry
	C	H	N	S[a]	Cl	M[b]	
$[MnCl_2(NSA)_2]$	35.3	2.4	6.7	16.1	18.1	13.4	Tetrahedral
	(35.6)	(2.5)	(6.9)	(15.8)	(17.8)	(13.6)	
$[FeCl_2(PPh_3)(NSA)]$	54.2	3.6	2.4	6.2	13.8	10.3	-do-
	(54.6)	(3.8)	(2.7)	(6.1)	(13.5)	(10.6)	
$[RuCl_2(PPh_3)_2(NSA)_2]$	58.8	3.7	3.2	6.5	7.6	—	Octahedral
	(59.1)	(4.1)	(2.9)	(6.6)	(7.3)	—	
$[RuCl_2(AsPh_3)_2(NSA)_2]$	54.4	3.4	2.4	5.6	7.0	—	-do-
	(54.2)	(3.8)	(2.6)	(6.0)	(6.7)	—	
$[CoH(P(OPh)_3)_2(NSA)]$	61.4	4.1	2.0	4.2	—	7.0	Square planar
	(61.5)	(4.4)	(1.7)	(3.9)	—	(7.2)	
$[RhCl(PPh_3)(NSA)_2]$	53.3	3.5	4.4	9.8	5.6	—	-do-
	(53.0)	(3.7)	(4.1)	(9.4)	(5.3)	—	
$[Rh(CO)Cl(PPh_3)(NSA)]$	52.4	3.3	2.8	5.2	6.4	—	-do-
	(52.8)	(3.5)	(2.5)	(5.6)	(6.3)	—	
$[Ni(P(OP)_3)_2(NSA)_2]$	59.6	4.0	3.3	6.9	—	6.0	Tetrahedral
	(60.2)	(4.2)	(2.9)	(6.7)	—	(6.2)	
$[Pd(PPh_3)_2(NSA)_2]$	63.2	4.0	3.4	7.4	—	11.6	-do-
	(63.4)	(4.4)	(3.1)	(7.1)	—	(11.7)	
$[Pt(PPh_3)_2(NSA)_2]$	57.5	4.1	3.0	6.6	—	—	-do-
	(57.8)	(4.0)	(2.8)	(6.4)	—	—	
$[CuCl(PPh_3)_2(NSA)]$	65.8	4.2	2.0	4.4	5.0	8.3	Tetrahedral
	(66.1)	(4.6)	(1.8)	(4.2)	(4.7)	(8.4)	
$[Ag(PPh_3)(NSA)](NO_3)$	50.1	3.3	5.1	5.7	—	18.7	Linear
	(50.4)	(3.5)	(4.9)	(5.6)	—	(18.9)	

[a] Sulphur was estimated as $BaSO_4$ after fusion of the complexes with sodium peroxide and potassium nitrate.
[b] Metal ions were estimated by standard methods[13a-c].

spectra of the ligand and complexes in chloroform were recorded on a Cary model 17-D spectrophotometer in the region 300-950 nm.

Melting points of the complexes are uncorrected and were observed on a Fisher-Johns melting point apparatus. Conductances of 10^{-3} *M* solutions of the complexes in nitrobenzene were measured using an Elico conductivity meter type CM-80.

Magnetic susceptibilities of the complexes were determined with the help of a Gouy balance at room temperature (25 ± 3°). Mercury tetrathiocyanatocobalt(II) was used as the calibrant; diamagnetic corrections were made as outlined by Figgis and Lewis[14].

Results and Discussion

The analytical data of the complexes (Table 1) correspond to the empirical formulae which suggest that the ligand is behaving as monodentate in all the complexes, if the preferential geometries which the metal ions adopt in their complexes are assumed[15]. Solubility of the complexes in most of the organic solvent indicates their monomeric nature.

The ligand has four sites for the metal bounding: (i) phenyl group as a whole which can form π-type of complexes with the metal ions by the overlap of π-orbitals of the phenyl group with the metal *d*-orbitals; and (ii) oxygen, sulphur and nitrogen atoms which can form complexes by the overlap of orbitals having paired non-bonding electrons with the appropriate metal orbitals. However, it is unlikely that the filled π-orbitals of the phenyl group or oxygen lone pair will take part in the bond formation, because of their relatively very low energies as compared to those of nitrogen and sulphur[1]. It is, therefore, assumed that the bonding of the ligand molecule with the metal ions takes place either with nitrogen or sulphur atom. In order to decide between these two alternatives, the infrared spectra of the ligand and its complexes were studied.

The infrared spectrum of NSA has been studied in detail by Stephenson *et al.*[2] on the assumption that NSA has C_s symmetry. We have followed the assignments as given by them. Besides the characteristic bands of the phenyl group which appeared in the spectra of the ligand as well as of the complexes, the IR spectrum of NSA exhibited two strong bands at 1158 and 1298 cm^{-1} assignable to two stretching vibrations of –NSO group; the three bands at 606, 438 and 411 cm^{-1} were assigned to –NSO in-plane, out-of-plane bending and –NSO in-plane wagging modes, respectively[2]. While studying the spectra of substituted phenyl analogues, Kresze and Maschke[16] have concluded that the phenyl π-electrons should be in conjugation with the π-electrons of the $-NSO$ group. Furthermore, in the stretching vibrational modes of the $-NSO$ group, the normal coordinates which give rise to these bands must also have a fair amount of contribution from $\nu(C=N)$ and $\nu(C=C)$. Kresze and Maschke have also pointed out that these contributions should be relatively more in the normal coordinate giving rise to 1298 cm^{-1} band than that to 1177 cm^{-1} band which may be having more contributions from $\nu(SO)$, $\nu(N=S)$ and other stretching modes of $-NSO$. In metal complexes, when the metal ions (electron-acceptors) interact with the nitrogen lone pairs, the contributions from the vibrational modes of $C=N$ and $N=S$ should, therefore increase in the normal coordinates. Thus, it is expected that on complexation, the position of the band at 1298 cm^{-1} should shift towards higher wavenumbers, while that at 1158 cm^{-1} should shift towards lower wavenumbers. The positions of the bands arising due to other bending modes should be slightly shifted. In addition, since the phenyl group is also participating in the resonating structures, some of the bands arising due to phenyl skeletal modes of vibration should also be shifted. The following are the major shifts in the band positions of $-NSO$ and some of those of the phenyl group:

(a) In the ligand spectrum, the bands assigned to phenyl group are present[2,15], at 1600, 1570, 1483, 1451, 1330, 1071, 1032, 1016, 998, 763, 750 and 682 cm^{-1}. While the bands at 1600, 1570, 1483, 1451 and 1330 cm^{-1} have shifted towards higher wavenumbers ($\sim +10$ cm^{-1}), those at 1071, 1032, 1016, 998, 763, 750 and 682 cm^{-1} have not shifted and the shifts in the positions of the remaining phenyl bands at lower wavenumbers are relatively small and variable (± 5 cm^{-1}). It indicates that possibly the positions of only those bands are shifted which have some contribution from $\nu(C=C)$ while the positions of those which have contributions from $C-H$ vibrational mode do not change. It is in conformity with the discussion in the foregoing paragraph.

(b) The ligand band at 1298 cm^{-1} shifted towards higher wavenumbers ($\sim +15$ cm^{-1}) in the spectra of all the complexes, suggesting the bonding of metal ions with the nitrogen atom of the NSO group.

(c) The position of the band at 1158 cm^{-1} shifted towards lower wavenumbers, (~ -20 cm^{-1}) in the spectra of all the complexes.

(d) The shifts in the positions of the bands at 636, 505 and 438 cm^{-1} in the spectra of the complexes could not be ascertained because of the presence of other weak and medium intensity bands in these regions. However, in the spectra of a few complexes 636 cm^{-1} band appeared to have shifted towards lower wavenumbers (~ 10 cm^{-1}).

(e) All the characteristic bands of triphenylphosphine were present in the spectra of the complexes of iron, ruthenium, rhodium, nickel, palladium, platinum, copper and silver. Further, the spectra of $[RuCl_2(AsPh_3)_2(NSA)_2]$ and $[CoH(P(OPh)_3)_2(NSA)]$, exhibited the characteristic bands of triphenylarsine and triphenylphosphite, respectively.

(f) The spectrum of $[Ag(PPh_3)(NSA)]$ (NO_3) exhibited all the characteristic bands of ionically bonded nitrate group.

(g) In the spectrum of $[Rh(CO)Cl(PPh_3)$ $(NSA)]$, the band appearing at 1960 cm^{-1} was assigned to $\nu(CO)$.

It is, therefore, concluded that the ligand is bonded to the metal ion through its nitrogen atom.

The complexes of Ru(II), Rh(I), Co(I), Ni(0), Pd(0), Pt(0), Cu(I) and Ag(I) were found to be diamagnetic. The diamagnetic behaviour of ruthenium(II) complexes clearly reveals that the metal ion exists as low spin d^6-system in both the complexes. In general, all the octahedral complexes of ruthenium(II), known till now, are diamagnetic[15b] and therefore, an octahedral geometry has been assigned to the complex. The diamagnetic behaviour of cobalt(I) and rhodium(I) (both belonging to d^6-system) indicates the expected preferred square planar geometry around the metal ions.

Since palladium(0), platinum(0), nickel(0) and copper(I) (d^{10}-system) complexes are four-coordinated, the only possible geometry that may be assigned to them is tetrahedral. The coordination number in the silver complex could be assigned as two (if NO_3^- ion is assumed to be ionic) or three (if NO_3 is assumed as coordinated). Since the complex is insoluble in water, its conductivity could not be determined and it is difficult to know the nature of bonding of silver ion with the nitrate group. However, in both the alternatives, the 4d-orbitals of silver ion are completely filled and one, therefore, expects the diamagnetic behaviour of the complex. Silver complexes, in general, are linear with coordination number two, and it is, therefore, assumed that the silver complex is also two-coordinated with nitrate ion as the counteranion. However, the possibility of the presence of three-coordinated silver ion also exists with nitrate forming rather a coordinate bond. nitrate ion acting as a bidentate in the complex is ruled out on the basis of infrared studies, where the positions of the NO_3^- bands did not correspond to the ones expected for bicoordinated NO_3^- ion.

The complexes of iron(II) and manganese(II) were found to be paramagnetic and exhibited magnetic moments of 5.18 and 5.8 B.M., which are typical of high spin species. Further, since the number of monodentate ligands around iron(II) ion in its complex is four, it is presumed that iron(II) forms four-coordinated tetrahedral high spin complex with NSA having triphenylphosphine and chloride ions as coligands. The magnetic moment value of 5.8 B.M. indicates the presence of five unpaired electrons. Since the analytical data suggest four monodentate ligands around the manganese ion, a tetrahedral geometry of the complex has been assumed.

The near UV spectrum of NSA displayed two absorption bands at 320 nm (31,250 cm $^{-1}$; log $\varepsilon = 3.90$) and 235 nm (42,553 cm $^{-1}$; log $\varepsilon = 3.80$). Leandri and Mangini[17], have assigned the low energy band to $n_{\mathrm{N_2}} \rightarrow \pi^*$ and the high energy one to $n_{\mathrm{S}} \rightarrow \pi^*$ transitions.

If one presumes that the bonding of the metal ion in the complexes takes place through the non-bonding lone pair in nitrogen atom, a part of the negative charge is removed from nitrogen atom. As a consequence, the effective electronegativity of nitrogen will be raised slightly, and thus stabilising the non-bonding orbitals whose energy levels will be lowered after the formation of M-N bond. This situation will cause greater energy difference between non-bonding orbital of nitrogen and those of the π^* orbitals of NSO-group. As a result, one will expect a shift in the position of the 320 nm band towards shorter wavelength region. If, on the other hand, the bonding of the metal ion is assumed to be through sulphur of $-$NSO group, the non-bonding electrons on sulphur atom will be more stabilised, causing a shift in the position of the band due to $n_{\mathrm{S}} \rightarrow \pi^*$ transition towards shorter wavelength. Experimentally, it is observed that the position of the band due to $n_{\mathrm{N_2}} \rightarrow \pi^*$ transition has been shifted towards lower wavelength (~ -10 cm $^{-1}$). Bonding of the metal ion is therefore assumed to involve the nitrogen atom of the ligand.

In the spectra of those complexes having triphenylphosphine or triphenylarsine as coligands, one or two bands in the 270 nm region have been observed. These are characteristic $\pi - \pi^*$ transition bands of the phenyl group of phosphine. The splitting of this band into two may be due to interligand interaction of the π or π^* levels.

In the spectra of all the complexes, a continuous intense absorption was observed starting from 550 nm onward. The very high intensity suggests that the band could not possibly be due to *d-d* transition, but it may either arise due to charge transfer or it may be due to the presence of intraligand band. Since the continuous absorption was observed both in the spectra of d^{10}-system, as well as that of the ligand, it is assumed that the continuous absorption is due to intraligand transition.

All the *d-d* transition bands which appear in wavelength region lower than 500 nm (20,000 cm $^{-1}$) were masked by the intense continuous absorption and hence no *d-d* transition bands were observed in the spectra of the complexes. However, a weak band appeared at 550 nm in the spectrum of Ru(II) arsine complex. This has been assigned to $^1T_{2g} \rightarrow {}^1A_{1g}$ transition, indicating the octahedral geometry[18]. No information regarding the stereochemistry of other complexes could, therefore, be inferred from the visible spectral data. However, in the complexes of the d^{10}-metal ions one does not expect any band in the visible region.

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