Monatshefte für Chemie 106, 1375—1380 (1975)

Schiff Base of O-Methylthioaniline and Salicylaldehyde and Its Metal Chelates

By

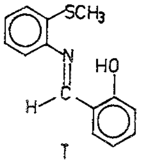
Ram Chand Paul, Sham Kumar Vasisht, Satish Kumar Mehra, and Dalbara Singh
Department of Chemistry, Panjab University, Chandigarh, India

(Received May 22, 1975)

The Schiff base salicylideneamino-o-methylthiobenzene (I), $CH_3S—C_6H_4—N=CH—C_6H_4—OH$ (*SMeNO*H), has been synthesized and its complexes of the type $CuX(SMeNO)$ where X = Cl, Br, NO_3, CNS, and ClO_4, $CuX'(SMeNOH)$ where $X' = SO_4$ and $(BF_4)_2$, $NiX''_2(SMeNOH)$ where X'' = Cl and Br, $NiNO_3(SMeNO)$ and $M(SMeNO)_2$ where M = Cu, Ni and Co, have been prepared and characterised through infrared, magnetic moment and conductance measurements.

Introduction

Chelating agents with sulphur and nitrogen sets of donors have been studied quite extensively but tridentates containing sulphur, nitrogen and oxygen as bonding sites have received much less attention[1]. One such Schiff base, salicylideneamino-o-methylthiobenzene (*SMeNO*H) (I) containing "etherial" sulphur, tertiary nitrogen and phenolic oxygen has been synthesized and its complexes with a variety of copper(II) salts and some nickel and cobalt salts have been prepared and studied.



I

Experimental

The solvents used were purified and dried by standard methods. Analytical grades of hydrated metal salts were used as such.

Salicylideneamino-o-methylthiobenzene (I): Equimolar quantities of o-methylthioaniline and salicylaldehyde were refluxed in ethanol for 3–4 hours.

The mixture was cooled, the solid formed was crystallised at least twice from ethanol; yellow needles, melting at 53 °C.

$C_{14}H_{13}NOS$. Found C 68.40, H 5.25, N 5.66.
Calcd. C 69.13, H 5.34, N 5.76.

Complexes of copper(II) chloride, bromide, nitrate, sulphate, and perchlorate were prepared by mixing equimolar amounts of the copper salt and the ligand I in hot ethanol. Stirring at room temperature precipitated the complexes which were filtered, washed with ethanol and dried under vacuum.

Complexes of nickel(II) chloride, bromide and nitrate were made by refluxing for 2–3 hours, an equimolar mixture of the salt and the ligand I in ethanol. Complexes of the type $M(SMeNO)_2$ were obtained by refluxing copper acetate, nickel acetate and cobalt chloride with the ligand I in the molar ratio 1 : 2 in ethanol.

Copper tetrafluoroborate-hexahydrate was stirred in excess of ethyl orthoformate with an equivalent amount of the ligand in ether at room temperature and the complex $Cu(BF_4)_2(SMeNOH)$ was filtered, washed successively with petroleum ether, ether and finally dried in vacuum.

In the case of $CuCNS(SMeNO)$, the equimolar mixture of copper nitrate-hexahydrate and ligand in ethanol was treated with KCNS solution in water. The solid separated was filtered and washed with water and then with alcohol and finally dried under vacuum.

Analysis

The complex was broken by repeatedly heating to almost dryness first with conc. HNO_3 and then with conc. HCl. The residue was then dissolved in water and copper was estimated gravimetrically as CuS and iodometrically by titration against $Na_2S_2O_3$. Nickel was estimated complexometrically by titration against *EDTA* using murexide as indicator. Cobalt was determined as $Co(C_5H_5N)_2(CNS)_2$.

Physical Measurements

Magnetic susceptibility was measured by the *Gouy* method employing $Hg[Co(NCS)_4]$ as standard. Molar conductance was measured on a conductivity bridge type CL 01/01. The infrared spectra were recorded as nujol mulls and as KBr pellets on Perkin Elmer 337 grating spectrophotometer. Nuclear magnetic resonance spectrum was recorded on Varian A 60 A using TMS as internal standard.

Results and Discussion

The Schiff base salicylideneamino-o-methylthiobenzene (*SMeNO*H) (I) shows important infrared bands at 3,405 and 1,610 cm^{-1} assigned to ν OH and ν C=N resp. The proton nmr spectrum of I in CCl_4 shows three sharp singlets at — 2.31, — 8.47 and — 12.70 ppm in the ratio 3 : 1 : 1 corresponding to SCH_3, CH and OH groups resp. A multiplet due to phenyl groups has been observed at — 7.07 ppm. The molecule is normally expected to behave as a negatively charged tridentate by the loss of a proton from the phenolic group and coordination through sulphur and tertiary nitrogen.

The interaction of copper halides with I produces complexes $CuX(SMeNO)$ where $X = Cl$ and Br. The infrared spectra show the absence of ν OH and the appearance of a band at 1,535 cm^{-1} due to ν C—O. It corresponds to nonbridging oxygen as already observed in complexes of certain Schiff bases[2]. The spectra of bi- and tri-nuclear oxobridged complexes show[3] ν C—O usually in the range 1,545–1,560 cm^{-1}. The magnetic moments of chloro and bromo complexes are 1.91 and 2.09 μ_B resp. These are normal values and speak for mononuclear copper(II) complexes. Consequently these, in analogy with similar known compounds, may be assigned the expected four coordinated mononuclear arrangement with the ligand acting as tridentate and the halogen atom occupying the fourth position. The chloride complex is nonpolar ($\Delta_{1000} = 4.1$ cm^2 ohm^{-1} $mole^{-1}$), whereas, the other one has a conductance 21.0 cm^2 ohm^{-1} $mole^{-1}$ (Uniuni-valent electrolyte 75–95 cm^2 ohm^{-1} $mole^{-1}$)[4] indicating a slight ionic character in the metal bromine bond in nitromethane solutions.

Nickel(II) halides, on the other hand, provide complexes $NiX_2(SMeNOH)$ where $X = Cl$ and Br. The i. r. spectrum of $NiCl_2(SMeNOH)$ shows the ν OH band at 3,405 and a weak absorption at 3,530 cm^{-1} showing that the phenolic group remains uncoordinated. In the bromo complex, however, the ν OH is found at 3,350 cm^{-1} and this lowering of 55 cm^{-1} shows its interaction towards metal. The former has a magnetic moment 3.32 and the latter 3.50 μ_B. These values are typical of an octahedral geometry which is possibly attained by polymerisation through halogen atoms[5]. Both the complexes are almost nonpolar in nitromethane (Table 1).

The light blue complex $CuSCN(SMeNO)$ shows infrared bands at 2,140 (ν CN), 470 (δ NCS) and 720 cm^{-1} (ν CS) which when compared with the values in literature[6] indicates that the thiocyanate group is bonded through its sulphur atom to metal. The ν C—O band at 1,535 cm^{-1} and the magnetic moment, 2.0 μ_B, as earlier stated are indicative of four coordinated non-oxo-bridging structure for the complex. The molar conductance in dimethylsulphoxide (*DMSO*) is 34.0 cm^2 ohm^{-1} $mole^{-1}$ and this value may be taken as the lower limit for uniuni-valent electrolytes[4]. The thiocyanate group perhaps becomes labile in the presence of a strong base like $DMSO[Cu(SMeNO)OSMe_2]^+SCN^-$.

The black complex $CuNO_3(SMeNO)$ shows infrared bands at 1,480 and 1,270 cm^{-1} showing that the nitrato group is coordinated and further ν NO has been observed[7] at 1,032 cm^{-1}. Just like in the already mentioned copper complexes the ν C—O band has been found at 1,535 cm^{-1}

and the magnetic moment is 1.80 μ_B. The complex has a slight polarity in nitromethane (Table 1).

The nickel complex $NiNO_3$(*SMeNO*) shows nitrate bands at 1,500 and 1,290 cm^{-1} due perhaps to its bidentate coordination to metal[5]. The

Table 1

No.	Compound	Colour	μ_{eff}, μ_B	M. Cond.* Λ 1000 (25°)	Analyses, % Calcd. Found				
					Metal	C	H	N	Hal.
I	CuCl(*SMeNO*)	Green	1.91	4.1^a	18.62	49.26	3.52	4.10	10.41
		black			18.40	48.68	3.38	4.27	10.02
II	CuBr(*SMeNO*)	Black	2.09	21.0^a	16.47	43.58	3.11	3.63	20.75
					16.28	41.89	2.98	3.39	19.90
III	$NiCl_2$(*SMeNO*H)	Yellow	3.32	7.2^a	15.74	45.07	3.49	3.75	19.05
		green			16.10	44.21	3.44	3.56	19.60
IV	$NiBr_2$(*SMeNO*H)	Yellow	3.50	14.5^a	12.71	36.38	2.81	3.03	34.65
		green			12.60	35.88	2.62	2.89	33.81
V	CuSCN(*SMeNO*)	Light	2.04	34.0^b	17.47	49.52	3.30	7.70	—
		blue			17.12	48.89	3.12	7.58	—
VI	$CuNO_3$(*SMeNO*)	Black	1.80	21.5^a	17.28	45.71	3.26	7.62	—
					16.88	44.90	3.19	7.81	—
VII	$NiNO_3$(*SMeNO*)	Yellow	3.05	16.0^b	16.18	46.32	3.31	7.72	—
		green			15.86	44.98	3.08	7.44	—
VIII	$CuClO_4$(*SMeNO*)	Green	1.68	14.5^c	15.68	41.48	2.96	3.45	—
					15.39	41.08	2.88	3.31	—
IX	$CuSO_4$(*SMeNO*H)	Green	2.30	20.6^d	15.77	41.74	3.23	3.48	—
					15.25	41.21	3.16	3.28	—
X	$Cu(BF_4)_2$(*SMeNO*H)	Light	1.84	142.2^a	13.21	34.96	2.70	2.91	—
		green			12.99	34.12	2.49	2.76	—
XI	Cu(*SMeNO*)$_2$	Dark	1.96	1.2^a	11.60	61.37	4.38	5.11	—
		green			11.25	60.12	4.21	4.78	—
XII	Ni(*SMeNO*)$_2$	Brown	3.23	7.3^a	10.81	61.91	4.42	5.16	—
					10.28	60.64	4.55	4.94	—
XIII	Co(*SMeNO*)$_2$	Dark	2.20	4.0^a	10.85	61.89	4.42	5.16	—
		green			10.17	61.20	4.08	4.82	—

* cm^2 ohm^{-1} mole^{-1}.

[a] nitromethane, [b] dimethylsulphoxide, [c] nitrobenzene, [d] dimethylformamide.

ν C—O has, however, been observed at 1,555 cm^{-1}, thereby, showing the existence of oxobridges in the complex[3]. The magnetic moment, 3.05 μ_B, shows an octahedral geometry. The conductivity 16.0 cm^2 ohm^{-1} mole^{-1} is much below the values for uniuni-valent electrolytes[4] and may be due to some decomposition of the complex in *DMSO*.

Copper perchlorate forms a green complex $CuClO_4$(*SMeNO*) which shows typical vibrations[8] of a coordinated perchlorato group at 1,140 and 1,090 cm^{-1}. A band at 1,535 cm^{-1} due to ν C—O shows absence of any oxygen bridging. The magnetic moment, 1.68 μ_B, is at the low end of the normal range usually found for copper complexes. The conductance 14.5 cm^2 ohm^{-1} mole^{-1} in nitrobenzene is, nodoubt, lower than the value (20—30 cm^2 ohm^{-1} mole^{-1}) for uniuni-valent electrolytes but shows appreciable ionic dissociation of the complex.

Table 2

Compound	ν OH	ν C=N	ν C—O	Anion vibrations			
				ν 1	ν 2	ν 3	ν 4
Ligand	3405 bm	1610 s	—	—	—	—	—
I	—	1610 s	1535 s	—	—	—	—
II	—	1610 s	1535 s	—	—	—	—
III	3530 w, 3405 m	1610 s	—	—	—	—	—
IV	3350	1610 s	—	—	—	—	—
V	—	1610 s	1535 s	2140 s	470 w	720 w	—
VI	—	1610 s	1535 s	1032 s	800 m	1480 s, 1270 s	750 m
VII	—	1610 s	1555 s	1030 s	800 m	1500 s, 1290 s	745 m
VIII	—	1610 s	1535 s	920 m	660 w	1140 s, 1090 s	625 m
IX	3300 s, 3200 to 3150 bs	1610 s	—	998 w	440 m	1110 s, 1045 s	640 s
X	3405 bm	1610 s	—	765 s	—	1110 sh, 1095 s, 1050 s	530 m, 518 m
XI	—	1605 s	1530 s	—	—	—	—
XII	—	1605 s	1530 s	—	—	—	—
XIII	—	1605 s	1530 s	—	—	—	—

s = Strong; m = Medium; w = Weak; bs = Broad strong; bm = Broad medium; sh = Shoulder.

Copper sulphate provides a green complex $CuSO_4$(*SMeNO*H) which shows strong infrared bands at 3,300 and 3,200—3,150 cm^{-1} assigned to OH stretching modes. This band in the ligand is found at 3,405 cm^{-1} and thus a lowering of about 100 cm^{-1} shows that the phenolic oxygen is coordinated to the metal atom. The infrared bands of the polyanion have been observed at 1,110 and 1,045 cm^{-1}, thereby, showing the existence of monodentate sulphato group[9]. Other bands of sulphato group (Table 1) confirm this. The magnetic moment, 2.20 μ_B, is normal as in other complexes (Table 1). The molar conductance (Table 1) shows a slight ionic dissociation of the complex in *DMF*.

The light green complex $Cu(BF_4)_2(SMeNOH)$ shows a strong band at 3,405 cm^{-1} assigned to ν OH. Since no change has been observed in the OH stretching frequency even on complex formation, therefore, the phenolic group remains nonbonded in the complex. The polyanion region shows three bands at 1,110, 1,095 and 1,050 cm^{-1} arising as a result of splitting of ν_3 mode of the BF_4 group due to its coordination to copper[8]. This is further confirmed by the appearance of a strong band at 765 cm^{-1} (Table 2). The magnetic moment of the complex is 1.84 μ_B. The molar conductance of 142.2 cm^2 ohm^{-1} $mole^{-1}$ in nitromethane shows its behaviour as a uni-divalent electrolyte. It is not surprising that in nitromethane, the coordinated fluoroborate group becomes labile.

Copper acetate, nickel acetate and cobalt chloride form complexes $M(SMeNO)_2$. The infrared spectra show no bands in the ν OH region and there appears a band at 1,530 cm^{-1} due to ν C—O showing that oxygen is covalently bonded to metal. The magnetic moments of the complexes are 1.96 (Cu), 3.23 (Ni) and 2.20 (Co) μ_B showing an octahedral geometry in each case. The molar conductance values (Table 1) indicate their non-electrolytic nature.

It has been observed that copper salts form complexes quite easily with the Schiff base I and these are four coordinated, whereas, nickel complexes could not be isolated in all cases and the isolated ones possess octahedral geometry.

References

[1] *M. A. Ali* and *S. E. Livingstone*, Coordin. Chem. Rev. **13**, 101 (1974).

[2] *M. A. Ali, S. E. Livingstone*, and *D. J. Phillips*, Inorg. Chim. Acta **7**, 179, 531 (1973).

[3] *C. M. Harris* and *E. Sinn*, J. Inorg. Nucl. Chem. **30**, 2723 (1968).

[4] *W. J. Geary*, Coordin. Chem. Rev. **7**, 81 (1971).

[5] *P. S. K. Chia* and *S. E. Livingstone*, Austral. J. Chem. **22**, 1613 (1969).

[6] *A. Sabatini* and *I. Bertini*, Inorg. Chem. **4**, 959 (1965).

[7] *B. M. Gatehouse, S. E. Livingstone*, and *R. S. Nyholm*, J. Chem. Soc. **1957**, 4222.

[8] *I. M. Proctor, B. J. Hathaway*, and *P. Nicholls*, J. Chem. Soc. **1968**, 1678.

[9] *K. Nakamoto, J. Fujita, S. Tanaka*, and *M. Kobayashi*, J. Amer. Chem. Soc. **79**, 4904 (1957).

Correspondence and reprints:
Dr. S. K. Vasisht
Department of Chemistry
Panjab University
Chandigarh 160014
India