

Studies on the Adducts of *p*-Toluidine with Copper(II) & Nickel(II) Sulphates & Their Reactions with Acetylhalides

S B KULKARNI, G N NATU*, S A RUIKAR† & H O DEORE‡

Department of Chemistry, University of Poona, Pune 411 007

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Reactions of the *p*-toluidine adducts of MSO_4 [$\text{M} = \text{Cu(II)}, \text{Ni(II)}$] with acetyl halides have been studied. The compounds obtained have been characterised on the basis of elemental analyses, magnetic moment, electronic, IR and ESR spectral data. It is observed that acetylation of the amine group of *p*-toluidine is not affected by coordination. Sulphato group is present as a bridging group. ESR studies show that the parent adduct, $\text{CuSO}_4(\text{ptol})_2 \cdot \text{H}_2\text{O}$, has an axially elongated site symmetry while its reaction products with acetyl halides have an axially compressed site symmetry.

Organic amines form an interesting series of adducts with many transition metal halides¹. In contrast to numerous reports available in literature on metal halide adducts, there are only a few reports on the adducts of copper(II) sulphate²⁻⁵ and still less on those of nickel(II) sulphate. We report here the results of our studies on $\text{M}(\text{ptol})_2 \cdot \text{SO}_4$, $\text{M} = \text{Cu(II)}, \text{Ni(II)}$; *ptol* = *p*-toluidine, and their reaction products with acetyl halides. The compounds have been characterized using electronic spectral, infrared spectral and magnetic susceptibility techniques; ESR spectra of copper(II) adduct and its reaction products are also reported in this work. Further, the effect of coordination on the acetylation of the amine is investigated.

Materials and Methods

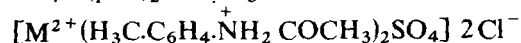
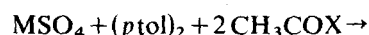
All the chemicals used were BDH reagents of LR grade. The adducts, $[\text{M}(\text{ptol})_2 \cdot \text{SO}_4]$, were prepared by the reported method². These adducts were subjected to reactions with acetyl halides under the experimental conditions stated elsewhere⁶.

All the products were analysed using standard methods. Elemental analyses for C, H and N were carried out at the Microanalytical Laboratory of the Department of Chemistry, University of Poona. Electrical conductivities in solution were measured on a Philips GM4144 conductivity bridge. TG studies were performed on a manually operated thermo-balance set in the authors' laboratory using Mettler P160 top loading balance of 1 mg accuracy. About 100 mg sample and a heating rate of 3°C/min were used. Electronic spectra of the compounds were recorded on a Beckman DK2 spectrophotometer; IR

spectra were recorded on a Perkin-Elmer 337 spectrophotometer in nujol and the ESR spectra of the copper(II) compounds were recorded on a Varian E-4 instrument (IIT, Madras). Assignments of the electronic spectral transitions are based upon the curve fitting programmes developed in the authors' laboratory⁷.

Results and Discussion

Data on elemental analysis and general physical properties are given in Table 1. The parent complexes have the compositions $\text{NiSO}_4(\text{ptol})_2$ and $\text{CuSO}_4(\text{ptol})_2 \cdot \text{H}_2\text{O}$. Acetylhalides combine with the parent adducts in the ratio 1:2. It is conceivable on the basis of the amine groups present in the parent compounds, that each amine will react with one acetyl group. Thus, the parent adduct of *p*-tol with MSO_4 changes to an adduct of *p*-toluamide with MSO_4 . The liberated HX during acetylation reaction seems to remain associated with the reaction product either as a quaternary ammonium salt or in an H-bonded form to the coordinated SO_4^{2-} group (Scheme 1).

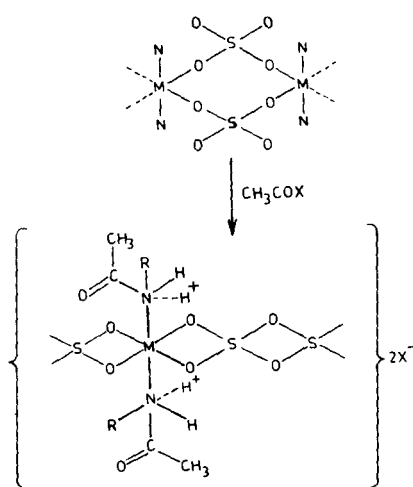


The single water molecule appears to be lost during the reaction of the copper adduct with acetyl halides. The solution conductivity data in dimethylformamide show a nearly non-electrolytic nature of the parent complexes. The reaction products, however, show a 1:1 electrolytic behaviour⁸ for reaction products with nickel(II) adduct and 1:2 type behaviour for the reaction products with copper(II) adducts.

TG studies on the parent compounds show that both the complexes decompose in the low temperature region of 50-180°C giving off 0.5 mol of *p*-toluidine per formula weight of the compound. The water molecule

† Present address: R.Y.K. Science College, Nasik 422 005.

‡ Present address: Pratap College, Amalner 425 401.



Scheme 1

in the copper(II) adduct is also expelled in the same temperature region. The other *p*-toluidine molecule is not expelled in the next step, instead a residue of uncertain composition is obtained.

The reaction products with acetyl halides give off *p*-toluamide ($\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3$) in the temperature region 50–180°C. In another step a molecule of hydrogen halide is expelled. The probable explanation for the expulsion of *p*-toluamide before HX could be the association of H^+ with SO_4^{2-} through H-bonding and that of X^- to metal ion. It is wellknown that H-bonded water molecules, even from metal salt hydrates, are often removed at high temperatures. The expulsion of *p*-toluamide was confirmed from its m.p.

(153°C)⁹ and IR spectrum. These observations reveal that *p*-toluamide also may be coordinated with metal ions in the solid state probably through oxygen and nitrogen; this was confirmed from the infrared spectral studies.

IR spectra of the parent adducts and their reaction products with acetyl halides have been compared to assign the mode of bonding in the reaction products. The pertinent data on important group frequencies have been presented in Table 2. The IR data for the reaction products with acetyl halides are comparable with each other for copper(II) as well as for nickel(II) compounds. However, the ν_3 vibrations associated with sulphato group in copper(II) reaction products were found to be at higher frequencies by about 30 cm^{-1} as compared with those for the nickel(II) compounds. This indicates that the interaction of the sulphato group with nickel(II) is stronger than that with copper(II). The IR spectra show that the sulphato group is coordinated to metal ion, probably as a bridging group, because the four degenerate vibrational modes of SO_4^{2-} (T_d) split into eight-fold non-degenerate vibrations (C_{2v}). Similar reports on cobalt-amine-sulphato complexes are known⁵. The formation of *p*-toluamide, as confirmed from the IR spectra, supports the observations of Fernando¹⁰ that coordination does not necessarily affect the substitution reaction of an organic ligand. The absorption bands of the other organic groups are quite comparable with each other as well as with those of the reaction products with copper(II) and nickel(II).

The electronic spectra of the parent adducts are reported in the literature^{2,3}. However, the pertinent

Table 1—Elemental Analysis and General Physical Properties of the Complexes

Compound (Form. Wt.)	Found (Calc.), %				$\Lambda/\text{ohm}^{-1}\cdot\text{mol}^{-1}\text{cm}^2$ in DMF
	M	N	SO_4^{2-}	X	
1 $\text{CuSO}_4\cdot(\text{ptol})_2\cdot\text{H}_2\text{O}$ (391.5)	17.12 (16.2)	6.8 (7.1)	25.0 (24.5)	—	30.4
2 $\text{NiSO}_4\cdot(\text{ptol})_2$ (368.7)	15.85 (15.92)	7.52 (7.59)	25.8 (26.04)	—	10.0
3 $[\text{CuSO}_4\cdot(\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{CO}\cdot\text{CH}_3)_2^+\cdot\text{Cl}_2^-]$ (530.5)	11.6 (11.9)	5.1 (5.3)	18.3 (18.0)	13.1 (13.4)	133.6
4 $[\text{CuSO}_4\cdot(\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{CO}\cdot\text{CH}_3)_2^+\cdot\text{Br}_2^-]$ (619.5)	10.5 (10.2)	4.1 (4.5)	15.3 (15.5)	25.6 (25.8)	168.1
5 $[\text{CuSO}_4\cdot(\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{CO}\cdot\text{CH}_3)_2^+\cdot\text{I}_2^-]$ (713.5)	8.8 (8.9)	3.7 (3.9)	13.2 (13.4)	35.3 (35.6)	159.8
6 $[\text{NiSO}_4\cdot(\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{CO}\cdot\text{CH}_3)_2^+\cdot\text{Cl}_2^-]$ (525.7)	11.0 (11.2)	5.2 (5.3)	17.8 (18.3)	13.0 (13.6)	90.0
7 $[\text{NiSO}_4\cdot(\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{CO}\cdot\text{CH}_3)_2^+\cdot\text{Br}_2^-]$ (614.7)	9.2 (9.6)	4.6 (4.5)	15.2 (15.6)	35.8 (36.0)	98.0
8 $[\text{NiSO}_4\cdot(\text{H}_3\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{CO}\cdot\text{CH}_3)_2^+\cdot\text{I}_2^-]$ (708.7)	8.1 (8.3)	3.8 (3.9)	13.0 (13.5)	35.6 (35.8)	58.3

Satisfactory C and H analyses were also obtained.

Table 2—IR Data (cm^{-1}) on the Adducts and Their Reaction Products

Compound	Group frequencies associated with				
	SO_4^{2-}	NH_2	C-N	C=O	M-N/M-O
<i>p</i> -toluidine	—	3400 (m) 3310 (s) 3200 (w) 1600 (s)	1280 (s) 1265 (s)	—	—
<i>p</i> -toluamide	—	3350 (s, b) 1620 (w)	1200 (s)	1580 (s)	—
$\text{CuSO}_4(\text{ptol})_2 \cdot \text{H}_2\text{O}$	1165 (s) 1105 (s) 1025 (s) 1005 (m) 645 (s) 580 (s) 480 (w)	3350 (s) 3140 (m) 1625 (s)	— 1185 (w)	—	—
$\text{NiSO}_4(\text{ptol})_2$	1120 (s) 1090 (s) 990 (m) 655 (s) 580 (s) 480 (w)	3320 (sh) 3260 (sh) 1570 (s)	1230 (m) 1200 (w)	—	685 (w) 525 (w)
$[\text{CuSO}_4(\text{H}_3\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{CO} \cdot \text{CH}_3)_2^+ \text{Cl}_2^-]$	1120 (s) 1090 (s) 590 (sd)	3350 (s, b) 1610 (m)	1200 (m)	1585 (s)	—
$[\text{NiSO}_4(\text{H}_3\text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 \cdot \text{CO} \cdot \text{CH}_3)_2^+ \text{Cl}_2^-]$	1090 (s, b) 615 (b) 490 (m)	3400 (b)	1255 (w) 1208 (m)	1580 (s)	480 (sh) 440 (b)

data seem to have been treated superficially. The spectrum of $\text{NiSO}_4(\text{ptol})_2$ exhibits two spin-forbidden bands. It is also known that whenever the energy ratio D_q/B approaches unity, the ν_3 transition appears as a well-defined doublet¹¹. The splitting of the ν_2 and ν_3 transitions may occur due to lowering of the symmetry from octahedral¹¹, due to spin-orbit coupling or intensity stealing mechanism.

The spectral data in Table 3 reveal the following aspects:

(i) The transition energy ratio D_q/B lies close to 1.0, indicating the splitting of spin-forbidden transition for the parent compound and its reaction products, ${}^3A_{2g} \rightarrow {}^1E_g$ and ${}^3A_{2g} \rightarrow {}^1T_{1g}$ for nickel(II).

(ii) The observed transition energy ratios ν_3/ν_1 , ν_3/ν_2 and ν_2/ν_1 lie in the ranges¹¹ 2.5-3.5, 1.5-2.0, and 1.5-1.7 respectively. This supports the octahedral site symmetry of the ligand field around nickel(II).

(iii) The calculated¹² and observed transition energies agree satisfactorily and the magnitudes of spectrochemical and nephelauxetic parameters fall in the normal ranges.

The electronic spectrum of the copper(II) sulphate adduct could be similarly explained (Table 4). In spite of an extensive spectral work on copper(II) complexes, there remains an uncertainty in the accurate assignments of electronic spectral transitions¹¹.

Assignments in the present work are based on the constancy of the ratio of tetragonality parameters¹², D_s and D_t (Table 4).

The parent compounds as well as their reaction products are paramagnetic. The nickel(II) compounds showed magnetic susceptibilities in the usual range for octahedral compounds. The magnetic moments calculated on the basis of ${}^3A_{2g}$ ground state of nickel and using the corresponding transition energies from electronic spectra¹³ were comparable with the observed values.

The copper(II) complexes are ideally suited for investigating the structure and the magnetic properties using ESR technique. Hathaway¹⁴ has extensively studied this aspect from the point of view of the axial distortions and the line shapes in ESR. The ESR spectrum of the parent copper (II) compound, $\text{CuSO}_4(\text{ptol})_2 \cdot \text{H}_2\text{O}$, exhibits a typically axially elongated site symmetry with g_{\parallel} and g_{\perp} values of 2.29 and 2.05 G respectively. This suggests a magnetic moment of 1.85 B.M. while the observed moment is 1.89 B.M. It is interesting to note that ESR spectra of all the reaction products show evidence of the axially compressed geometry. The addition reaction with acetyl halide converts the amine in *p*-tol to amide group. This is responsible for weakening of the bonding between copper(II) and amide nitrogen which

Table 3—Electronic Spectral Data (cm^{-1}) of Nickel(II) Compounds

Parameter	Adduct	Reaction products with		
		$\text{NiSO}_4 \cdot (\text{ptol})_2$	CH_3COCl	CH_3COBr
ν_1 (${}^3A_{2g} \rightarrow {}^3T_{2g}$)	7690	8547	9090	8620
ν_2 (${}^3A_{2g} \rightarrow {}^3T_{1g}$)	13200 (12943)	13800 (14128)	13950 (14886)	14500 (14300)
ν_3 [${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$]	23750 (24390)	24000 (24691)	25000 (25316)	25000 (25310)
ν_1 (forbid.) (${}^3A_{2g} \rightarrow {}^1E_g$)	15500 (15150)	14800 (14220)	14700 (14035)	15000 (14800)
ν_2 (forbid.) (${}^3A_{2g} \rightarrow {}^1T_{1g}$)	21200 (20490)	22000 (20850)	22000 (21205)	21000 (21410)
ν_3/ν_1	3.17	2.88	2.78	2.93
ν_3/ν_2	1.88	1.74	1.70	1.76
ν_2/ν_1	1.68	1.65	1.63	1.65
D_q	769	854	909	862
(calc.)	(790)	(860)	(920)	(840)
B	950	878	862	917
D_q/B	0.8	0.97	1.05	0.93
β_{3s}	0.91	0.84	0.82	0.88
$\mu_{\text{obs.}}$ B.M.	3.26	3.19	3.19	3.19
(calc.)*	(3.29)	(3.24)	(3.22)	(3.24)

*From electronic spectral data.

Table 4—Electronic Spectral Data (cm^{-1}) and ESR Data on Copper(II) Compounds

Parameter	Adduct	Reaction products with		
		$\text{CuSO}_4 \cdot (\text{ptol})_2$	CH_3COCl	CH_3COBr
ν_1 (${}^2B_{1g} \rightarrow {}^2A_{1g}$)	9990	7850	7885	7740
ν_2 (${}^2B_{1g} \rightarrow {}^2B_{2g}$)	11430	9480	9525	9345
ν_3 (${}^2B_{1g} \rightarrow {}^2E_g$)	15870	13600	13510	13330
D_s	1635	1710	1696	1675
D_t	209	200	220	207
D_s/D_t	8.1	8.5	7.6	8.1
g_{\parallel}	2.29	2.05	2.03	2.01
g_{\perp}	2.06	2.13	2.25	2.28
$\mu_{\text{obs.}}$ B.M. (from ESR)	1.89 (1.85)	1.86 (1.83)	1.85 (1.89)	1.85 (1.89)

results in the weakening of axial interaction. Thus, the axially elongated configuration of the parent copper(II) adduct changes to axially compressed one. The line shapes for axially elongated and compressed configurations¹⁴ are quite typical such that $g_{\parallel} > g_{\perp}$ in magnitude for the former while $g_{\perp} > g_{\parallel}$ for the latter case. The line shapes of the ESR spectra in the present case conform to those reported¹⁴. Electronic spectra and magnetic studies are thus mutually supporting.

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