The Preparation and Properties of Some Aniline Complexes of Metal(II) Sulphates and Nitrates

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The complexes formed by aniline, *o*-, *m*-, and *p*-toluidine, and 3,4-, 2,5-, and 2,6-xylidine with manganese(II), iron(II), cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) sulphates and nitrates have been prepared. The complexes have been examined spectroscopically, and possible structures are discussed.

In previous Papers[1,2] details were given of complexes prepared from anilines and substituted anilines with metal(II) halides. Structures could be postulated for these on the basis of co-ordination from the anilines and the halides, and in many cases it was necessary to envisage the halogens as bridges. We now describe complexes formed from anilines with metal sulphates and nitrates.

TABLE 1

Sulphate complexes

			Found			Required		
Complex	Method of prepn.*	M–O band (cm.$^{-1}$)	Metal	SO_4^{2-}	Equiv. wt. loss	Metal	SO_4^{2-}	Equiv. wt. loss
$FeSO_4$,2An (*a*)	A	281	16·6	28·8	—	16·5	28·4	—
$FeSO_4$,2*p*-Tol	A	267	15·0	27·1	—	15·3	26·3	—
$CoSO_4$,2An (*b*)	A	278	16·9	28·5	—	17·3	28·1	—
$CoSO_4$,2·5*m*-Tol	B	—	13·6	22·9	—	14·0	22·7	—
$CoSO_4$,2*p*-Tol	A	266	15·6	26·7	—	16·0	26·0	—
$CoSO_4$,2(3,4-Xyl)	A	256	14·7	24·5	—	14·9	24·2	—
$NiSO_4$,2An (*c*)	A	281	17·0	28·0	—	17·3	28·1	—
$NiSO_4$,An	C	281	23·3	—	74	23·8	—	74
3($NiSO_4$),2An	C	—	26·7	—	99	27·2	—	96
$NiSO_4$,2*m*-Tol	A	263	15·5	25·5	—	16·0	26·0	—
3($NiSO_4$),2*m*-Tol	C	—	26·6	—	64	26·1	—	66
$NiSO_4$,2*p*-Tol	A	—	15·8	26·3	—	16·0	26·0	—
$NiSO_4$,*p*-Tol	C	—	23·1	—	160	22·5	—	160
2($NiSO_4$),5(3,4-Xyl)	A	270	12·9	22·0	—	12·9	21·0	—
$CuSO_4$,2An (*d*)	A	256	18·1	28·2	—	18·4	27·8	—
3($CuSO_4$),4An	C	—	22·3	—	44	22·4	—	44
$CuSO_4$,2*m*-Tol	A	256	16·6	25·4	—	17·0	25·7	—
3($CuSO_4$),4*m*-Tol	C	—	20·5	—	77	21·0	—	78
$CuSO_4$,2*p*-Tol	A	247	17·1	26·2	—	17·0	25·7	—
$CuSO_4$,2(3,4-Xyl)	A	260	15·8	23·8	—	15·8	23·9	—
$ZnSO_4$,2An (*e*)	A	253	18·6	28·4	—	18·8	27·6	—
$ZnSO_4$,An	C	264	26·4	38·3	91	25·7	37·7	90
$ZnSO_4$,2*m*-Tol	A	—	17·0	26·0	—	17·4	25·6	—
$ZnSO_4$,*m*-Tol	C	247	24·5	35·9	146	24·4	35·8	145
$ZnSO_4$,2*p*-Tol (*f*)	A	—	17·2	26·4	—	17·4	25·6	—
$ZnSO_4$,*p*-Tol	C	253	23·9	36·8	191	24·3	35·8	191
$ZnSO_4$,2(3,4-Xyl)	A	279	16·5	24·3	—	16·2	23·8	—
$ZnSO_4$,(3,4-Xyl)	C	253	22·6	33·7	50	23·1	34·0	50
$CdSO_4$,2An (*g*)	B	245	28·4	24·9	—	28·5	24·4	—
2($CdSO_4$),3An	A	246	31·2	27·7	—	32·4	27·7	—
$CdSO_4$,2*m*-Tol	A	—	16·6	25·4	—	17·0	25·7	—
$CdSO_4$,2*p*-Tol	A	—	26·0	23·3	—	26·6	22·7	—
$CdSO_4$,2(3,4-Xyl)	A	—	25·0	21·3	—	24·4	21·3	—

TABLE 1 (*Continued*)

Nitrate complexes

Complex	Method of prepn.*	M–O band (cm.$^{-1}$)	Found		Required	
			Metal	N	Metal	N
$Mn(NO_3)_2,2An$	D	258	15·0	15·1	15·0	15·3
$2[Mn(NO_3)_2],3o$-Tol	D	—	16·1	14·4	16·2	14·4
$Mn(NO_3)_2,2m$-Tol	D	253	14·3	13·3	14·0	14·2
$4[Mn(NO_3)_2],9p$-Tol	D	—	13·1	14·1	13·1	14·2
$Mn(NO_3)_2,2(3,4$-Xyl)	D	256	12·8	—	13·0	—
$2[Co(NO_3)_2],5An$	D	256	14·3	14·5	14·4	15·2
$Co(NO_3)_2,2o$-Tol	D	—	14·6	14·5	14·9	14·1
$Co(NO_3)_2,2m$-Tol	D	—	14·5	13·2	14·9	14·1
$Co(NO_3)_2,2p$-Tol (*e*)	D	256	15·0	14·6	14·9	14·1
$2[Co(NO_3)_2],5(3,4$-Xyl) (*k*)	D	255	12·0	—	12·1	—
$Ni(NO_3)_2,3An$	E	278	12·3	—	12·7	—
$Ni(NO_3)_2,4m$-Tol	E	—	9·4	—	9·6	—
$Ni(NO_3)_2,2p$-Tol	E	278	14·6	—	14·9	—
$Ni(NO_3)_2,4(2,5$-Xyl)	E	—	8·6	—	8·8	—
$Ni(NO_3)_2,3(3,4$-Xyl)	E	254	10·7	—	10·8	—
$Cu(NO_3)_2,4An$	F	267	11·4	14·5	11·3	15·0
$Cu(NO_3)_2,3o$-Tol	F	275, 253	12·6	13·1	12·5	13·7
$Cu(NO_3)_2,2m$-Tol	F	—	15·8	13·8	15·8	13·9
$Cu(NO_3)_2,2p$-Tol	F	282	15·7	13·7	15·8	13·9
$Cu(NO_3)_2,2(2,6$-Xyl)	F	—	14·5	12·7	14·8	13·0
$Cu(NO_3)_2,2(3,4$-Xyl)	F	—	14·3	—	14·8	—
$2[Zn(NO_3)_2],5An$ (*h*)	D	270	15·7	15·0	15·5	14·9
$Zn(NO_3)_2,2o$-Tol	D	—	16·3	13·3	16·2	13·9
$Zn(NO_3)_2,2m$-Tol	D	265	16·2	14·0	16·2	13·9
$Zn(NO_3)_2,3p$-Tol	D	—	12·8	13·3	12·8	13·7
$Zn(NO_3)_2,2(2,5$-Xyl)	D	255	14·9	12·1	15·1	13·0
$Zn(NO_3)_2,2(3,4$-Xyl)	D	258	14·8	—	15·1	—
$Cd(NO_3)_2,3An$ (*i*)	D	—	21·6	13·6	21·8	13·6
$Cd(NO_3)_2,3o$-Tol	D	—	20·0	12·4	20·1	12·5
$Cd(NO_3)_2,3m$-Tol	D	—	19·9	12·5	20·2	12·6
$Cd(NO_3)_2,3p$-Tol (*j*)	D	—	19·9	12·6	20·2	12·6
$Cd(NO_3)_2.3(2,5$-Xyl)	D	—	18·6	11·8	18·7	11·7
$4[Cd(NO_3)_2],9(2,6$-Xyl)	D	—	21·9	11·8	22·1	11·7
$Cd(NO_3)_2,3(3,4$-Xyl)	D	—	18·0	—	18·7	—

An = Aniline; Tol = Toluidine; Xyl = Xylidine.

* Methods of preparation: (A) metal sulphate plus the appropriate aniline; (B) metal sulphate plus the appropriate aniline in methanol; (C) thermal decomposition of the complex containing more ligand; (D) metal nitrate plus the appropriate aniline; (E) nickel nitrate plus the appropriate aniline in n-propanol; (F) copper nitrate plus the appropriate aniline in ethanol.

(*a*) Ref. 3. (*b*) A complex $CoSO_4,4An$ was reported previously but was not found in the present work. (*c*) Ref. 4. (*d*) Refs. 4 and 5; hydrates have been reported in this series.[5] (*e*) Refs. 4 and 6. (*f*) A complex $2ZnSO_4,3p$-Tol was reported previously [4,7] but was not found in the present work. (*g*) Ref. 8; no analytical data are given. (*h*) A complex $Zn(NO_3)_2,2An$ was reported previously.[4] (*i*) A complex $Cd(NO_3)_2,2An$ was reported previously.[6] (*j*) A complex $Cd(NO_3)_2,2p$-Tol was reported previously.[6] (*k*) Recrystallised from tetrahydrofuran.

The compounds prepared are summarised in Table 1, which contains references to previous preparations if the compounds are not new, together with analytical data and most of the preparative methods. Aniline complexes were described previously but the complexes of aniline derivatives are new. Many of the complexes prepared contain non-integral ratios of ligand molecules to metal atoms. The compounds are obtained reproducibly by using a given method of preparation but varying the ratios of reactants, and must be considered as definite chemical entities.

Iron(II) complexes are difficult to prepare, and we isolated only the aniline and *p*-toluidine derivatives of iron(II) sulphate. These change colour and are oxidised in air, and the failure to obtain a range of iron(II) complexes may be due to oxidation during the preparation. Manganese(II) sulphate forms no complexes with anilines, although manganese(II) nitrate forms a full range. Manganese(II) sulphate is virtually insoluble in anilines, and the aniline complexes of manganese(II) sulphate would not necessarily be unstable.

o-Toluidine and 2,5- and 2,6-xylidine have substituents adjacent to the co-ordinating amino group, and, if such factors are important in complexing, would be expected to show steric effects. These bases form complexes with nitrates only. The basicity of *o*-toluidine is lower than that of the other toluidines and is comparable with that of 2,6-xylidine (p*K* values:[9] aniline, 4·58; *o*-toluidine, 4·39; *m*-toluidine, 4·69, *p*-toluidine 5·12; 2,6-xylidine, 3·89), but there is also a steric factor in the relative basicities. These sterically

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[2] I. S. Ahuja, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Inorg. Nuclear Chem.*, 1965, **27**, 1625.

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[5] G. Gerhardt, *Compt. rend.*, 1845, **21**, 758; J. V. Dubsky and A. Rabas, *Coll. Trav. chim.*, 1929, **1**, 528.

[6] A. R. Leeds, *J. Amer. Chem. Soc.*, 1881, **3**, 134.

[7] B. Lachowitz, *Monatsh.*, 1889, **10**, 884, 895.

[8] J. C. Earl and N. G. Hills, *J. Chem. Soc.*, 1947, 973.

[9] A. Albert and E. P. Serjeant, "Ionisation Constants of Acids and Bases," Methuen, London, 1962.

hindered ligands form more nitrate complexes than sulphate complexes but the factors governing formation of specific species include the electron-donating ability of the oxyanion and the properties of the anilines as solvents, so the lack of formation of sulphate complexes may be fortuitous.

Most of the compounds prepared resulted from reactions in solution using the ligand as solvent, but it was possible to produce new complexes by heating the aniline–metal sulphate derivatives. Aniline–metal nitrate complexes decompose explosively when heated, and it was not possible to isolate intermediates during the decomposition.

The ultraviolet and visible reflectance spectra of the solid complexes have been measured over the range 300 mμ to 1 μ. The results (Table 2), taken in conjunction with the pale colours, are strongly in favour of octahedral co-ordination about the metal in the manganese, cobalt, and nickel complexes. The spectra of the iron(II) complexes in this region are not helpful in distinguishing between octahedral and tetrahedral co-ordination. The results for copper are consistent with tetragonally distorted environments about the metal atoms but do not exclude five-co-ordination or other non-regular co-ordination arrangements. The ultraviolet and visible spectra of the zinc and cadmium complexes give no indication of the environment about the metal atom.

TABLE 2

Ultraviolet and visible spectra (all figures in cm.$^{-1}$ × 10^{-3})

Manganese	$^4T_{1g}(G)$			
$Mn(NO_3)_2$,2An	18·2			
$[Mn(H_2O)_6]^{2+}$ *	18·9			
Iron	^5E_g			
$FeSO_4$,2An	11·1			
$FeSO_4$,2*p*-Tol	11·1			
$[Fe(H_2O)_6]^{2+}$ *	10·4	19·8, 21·1, 22·2 (triplets)		
Cobalt	^2E_g	$^4A_{2g}$	$^4T_{1g}$	
$CoSO_4$,2An	—	15·9	18·2, 17·8	
$2[CoSO_4]$,5*m*-Tol ...	—	15·5	17·2, 18·8	
$CoSO_4$,2*p*-Tol	—	15·4	17·6	
$CoSO_4$,2(3,4-Xyl) ...	—	15·4	17·1, 18·8	
$2[Co(NO_3)_2]$,5An ...	12·8	16·2	19·0	
$CoSO_4$,An	14·1(?)	15·9	18·2	
$[Co(H_2O)_6]^{2+}$ *	11·3	16·0	19·4, 21·5	
Nickel	$^3T_{1g}$	^1E_g	$^1T_{2g}$	$^3T_{1g}$
$NiSO_4$,2An	13·9	13·1(sh)	20·0(sh)	23·2
$NiSO_4$,2*m*-Tol	13·7	13·1(sh)	—	22·2
$NiSO_4$,2*p*-Tol	13·9	13·1(sh)	20·0(sh)	23·2
$2(NiSO_4)$,5(3,4-Xyl)	14·3	—	20·4(sh)	23·8
$Ni(NO_3)_2$,3An	15·1	—	—	—
$[Ni(H_2O)_6]^{2+}$ *	13·5	15·4(sh)	22·0(sh)	25·3
Copper				
$CuSO_4$,2An	11·3			
$CuSO_4$,2*m*-Tol	12·0			
$CuSO_4$,2*p*-Tol	14·7, 11·3			
$CuSO_4$,2(3,4-Xyl) ...	11·7			
$[Cu(H_2O)_6]^{2+}$ *	12·6			

Spectroscopic states correspond to transitions causing absorption.

* Values from C. K. Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon, Oxford, 1962.

If the evidence of the reflectance spectra is taken in conjunction with the stoicheiometries of the complexes, it is clear that the sulphate and nitrate groups must be co-ordinated to the metal atoms in all the manganese, iron, cobalt, and nickel complexes prepared in this work. It is not possible to make inferences as to the ligand-field effects of the sulphato and nitrato groups, as effects due to different arrangements of packing in the crystal lattices resulting from different stoicheiometries are likely to be far greater than ligand-field effects. Sulphato and nitrato complexes are well established. The anhydrous metal sulphates of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc are co-ordination polymers [10] with octahedral co-ordination about the metal atoms. Copper(II) nitrate, the only anhydrous nitrate of a first-row transition metal with a known structure, is also a co-ordination polymer, and each copper atom has eight nearest neighbours.[11]

Ideally, confirmation of the co-ordination by the sulphate and nitrate groups should be sought in their infrared spectra, where it should be possible to distinguish ionic, non-co-ordinated species, and co-ordinated species. However, this method is complicated by the difficulties of separating vibrations originating in the nitrate and sulphate groupings from those from the organic ligands. It is made even more difficult by the fact that the complexes are solids and all the infrared bands show considerable splittings due to site-symmetry effects. There is a wide range of different order of splitting of the infrared bands, but it can be stated definitely that the zinc and cadmium complexes show spectra which are very similar to those of manganese, cobalt, and nickel, and hence that the zinc and cadmium complexes probably contain metal atoms in octahedral co-ordination. The bands near to 1100 cm.$^{-1}$ which originate from sulphate or nitrate groups are broad but generally appear not to be split to any marked extent. This would be in agreement with regular co-ordination [12] from all the oxygen atoms of each sulphate and nitrate group to form co-ordination polymers. Since the basic lattice would then consist of the metal–oxyanion framework, the existence of complexes containing unusual ratios of organic ligand to metal atom would be explained on the basis of incorporation of the ligand on co-ordination sites throughout the lattice without materially altering the lattice. The ready loss of anilines from the metal sulphate complexes would be explained on a similar model, with the bridging network of sulphato groups closing up on thermal decomposition.

The far-infrared spectra of most of the complexes show strong bands near 250 cm.$^{-1}$ (Table 1), which appear to be derived from metal–sulphate and metal–nitrate modes. This frequency is much lower than that

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[10] J. D. Dunitz and P. Pauling, *Acta Cryst.*, 1965, **18**, 737.

[11] S. C. Wallwork, *Proc. Chem. Soc.*, 1959, 311.

[12] K. Nakamoto, " Infrared Spectra of Inorganic and Co-ation Compounds," Wiley, New York, London, 1963.

normally associated with metal–oxygen vibrations,[12] but the lowering is consistent with the presence of the oxyanions as bridges (cf. the lowering of metal–halide frequencies on bridging [13]).

EXPERIMENTAL

The details of the preparations are in Table 1. Samples were analysed for metal, and sulphate or nitrogen. Microanalyses for C and H confirm the formulations given in Table 1.

Thermal decomposition studies were carried out on a Stanton Thermal Balance working at a chart speed of 6 in./hr. All thermal decompositions were performed in air. After a thermal decomposition product had been recognised on the thermal balance, further samples were obtained by heating in an oven pre-set to the required temperature. Some of the thermal decompositions took place with slight charring, and in these cases it was not possible to obtain good spectra of the resultant complexes. Many of the thermal decomposition products were soluble only in concentrated sulphuric acid, so analysis could only be carried out for the metals.

Diffuse-reflectance spectra were taken for all materials on a Hilger Uvispek spectrophotometer in the range 300—1000 mμ. The details of selected spectra are in Table 2. Infrared spectra were recorded on a Perkin-Elmer Model 125, or a Grubb–Parsons D.M.2. spectrophotometer, for Nujol or hexachlorobutadiene mulls.

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