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Transition Metal Sulfate Complexes with 2,6-Lutidine N-Oxide and Triphenylphosphine Oxide*

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Synthetic and characterization studies of divalent 3d metal sulfate complexes with 2,6-lutidine N-oxide (LNO) and triphenylphosphine oxide (TPPO) are reported. $CoSO_4$ forms a hydrated 1:1 complex with LNO, involving ionic sulfate and a complex cation, which is probably of the type $[(H_2O)_4Co(LNO)_2Co(OH_2)_4]^{4+}$ with bridging LNO ligands. $Fe(LNO)(SO_4)$ and $Ni(LNO)_2(SO_4)$ involve chelating sulfato and bridging LNO ligands; probable formulations for these compounds are: $[(O_2SO_2)Fe(LNO)_2Fe(O_2SO_2)]$, a dimer with exclusively bridging LNO groups; and $[(O_2SO_2)(LNO)Ni(LNO)_2Ni(LNO)(O_2SO_2)]$, a binuclear pentacoordinated complex involving both terminal and bridging LNO ligands. $Cu(LNO)_2(SO_4)$ and $M(TPPO)_2(SO_4)$ (M = Fe, Ni) contain bridging bidentate sulfato ligands; the former complex was formulated as $[(LNO)_2Cu{-}(O{-}S(O_2){-}O){-}Cu(LNO)_2]$, a dimer with exclusively terminal LNO groups, whereas the latter compounds appear to be higher polymers, involving both terminal and bridging TPPO ligands, bridging bidentate sulfato ligands and coordination number five for the central metal ions. Attempts at the synthesis of $CoSO_4$ or $CuSO_4$ complexes with TPPO were unsuccessful.

Introduction

Complexes of aromatic amine N-oxides[1] and triorganophosphine oxides[2] with transition metal salts of a variety of inorganic anions (*e.g.*, halides, pseudohalides, nitrates, perchlorates, tetrafluoroborates) have been extensively studied, especially during the last 15 years. Nevertheless, little is known about transition metal sulfate complexes with ligands of these types. Thus, a 3:1 complex of triethylphosphine oxide with $CuSO_4$ was known as early as 1862,[3] while complexes of the type $ZnSO_4 \cdot L$ (L = pyridine N-oxide or 4-picoline N-oxide)[4] and adducts of $U(SO_4)_2$ with tri-n-butylphosphine oxide[5] were reported recently. We have recently reported synthetic and characterization studies of triphenylphosphine oxide (TPPO) complexes with metal perchlorates[6] and 2,6-lutidine N-oxide (LNO) complexes with metal perchlorates,[7] nitrates and thiocyanates.[8] It was of interest to us to explore the possibility of preparing and characterizing 3d metal sulfate complexes with the above ligands, and work in this direction was undertaken. The results of this study are reported in the present paper.

Experimental

J.T. Baker LNO and Carlisle Chemical Works TPPO were utilized; the purest commercially available hydrated metal sulfates and solvents were used. LNO complexes with Fe(II), Co(II), Ni(II) and Cu(II) sulfates were prepared as follows: the hydrated salt was dissolved in methanol and an excess of ligand was added to the solution; the great bulk of the solvent was allowed to evaporate (heating at *ca.* 80° C) and additional LNO was then added; the resulting mixture was, subsequently, gradually cooled to room temperature, under stirring, and the complexes were then precipitated by addition of anhydrous diethyl ether. The TPPO complexes with Fe(II) and Ni(II) sulfates were obtained by dissolving the hydrated salt in methanol, adding excess ligand, allowing the great bulk of the solvent to evaporate and precipitating the new complexes with ligroine (b. p. 63–75° C). Co(II) and Cu(II) sulfate complexes with TPPO were not obtained by this method or by a number of other synthetic approaches. The new complexes were filtered, washed with ether or ligroine and dried in an evacuated desiccator over phosphorus pentoxide. Characterization of the new complexes was based on spectral (ir–electronic), magnetic and conductance measurements, which were effected by methods previously described.[6–8] Analyses of the complexes were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

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TABLE I. Analytical Data for Metal Sulfate Complexes with LNO and TPPO.

Complex	Color	Analysis							
		C%		H%		N or P%		Metal %	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[Fe(LNO)(SO_4)]_2$	Brown	30.57	30.11	3.29	3.71	5.09	4.77	20.31	19.85
$[Fe(TPPO)_2(SO_4)]_x$	Pale yellow	61.03	61.22	4.27	4.42	8.74	8.79	7.88	8.17
$[Co(LNO)(OH_2)_n](SO_4)$[a]	Pink violet	24.01	24.56	4.88	4.55	4.00	3.94	16.85	17.29
$[Ni(LNO)_2(SO_4)]_2$	Yellow	41.92	42.53	4.52	4.84	6.98	6.81	14.63	14.12
$[Ni(TPPO)_2(SO_4)]_x$	Pale yellow	60.78	60.07	4.25	4.69	8.71	8.84	8.25	7.81
$[Cu(LNO)_2(SO_4)]_2$	Light green	41.41	40.84	4.47	4.61	6.90	6.73	15.65	16.04

[a] The calculated values correspond to the formula $[Co(LNO)(OH_2)_4](SO_4)$; n = 4 or 5 (see text).

TABLE II. Pertinent Infrared Data[a] for Metal Sulfate Complexes with LNO and TPPO (cm^{-1}).

Complex	$\nu(SO_4)$ modes[b]				ν_{X-O}(X = N or P)[c]	ν_{M-O} modes[e]
	ν_1	ν_2	ν_3	ν_4		
$[Fe(LNO)(SO_4)]_2$	987m–s, b	472m–s, sh	1255vs 1073vvs 1041s	640m 627m 601m–s	1197s	371m–w,* 311m, sh,$^+$ 298m, vb$^+$
$[Co(LNO)(OH_2)_n](SO_4)$	976w, sh	–	1124vs, vb	628s	(d)	330w, sh,‡ 308m, sh,* 280m–s, b*
$[Ni(LNO)_2(SO_4)]_2$	1002m	467m, sh	1233vs 1092vvs 1040s, sh	631s, sh 626s 590s	1207s	376m–s,* 358m* 321m,$^+$ 294m, sh
$[Cu(LNO)_2(SO_4)]_2$	990s	478m, sh	1200vs 1102vs, b 1030vs	659s 633s 581s	1217s	408s,* 320m–s,$^+$ 309m–s$^+$
$[Fe(TPPO)_2(SO_4)]_x$	1000s–m	451m	1194vs 1100s, 1076s	625m 600m, b	1121vs or (f) 1119vs	406m–s,* 360m, b,* 296m,$^+$ 284m$^+$
$[Ni(TPPO)_2(SO_4)]_x$	996s	459m	1187vs 1095s, sh 1072s	633m, sh 618m 601m, sh	1120vs or (f) 1114vs	404m–s,* 357m,* 291m,$^+$ 282m$^+$

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

[a] Recorded on Nujol mulls. [b] Labelling of the ν_{1-4} fundamental vibrations of ionic (T_d) sulfate after Nakamoto *et al.*[12]

[c] ν_{N-O} in free LNO: 1245 cm^{-1};[7] ν_{P-O} in free TPPO: 1195 cm^{-1}.[6] [d] Masked by the very strong and broad $\nu_3(SO_4)$ band.

[e] Tentative assignments of the primary character of the ν_{M-O} absorptions are made as follows (see text): * ν_{M-O} (ligand) (*i.e.*, LNO or TPPO); $^+\nu_{M-O}$ (sulfato); $^{\ddagger}\nu_{M-O}$ (aquo). [f] Overlapping ν_{P-O} and ν_{Ligand} bands.

Results

Analytical data, shown in Table I, suggest the following stoicheiometries for the new complexes: $Fe(LNO)(SO_4)$, $Co(LNO)SO_4 \cdot nH_2O$ (n = 4 or 5), $M(LNO)_2(SO_4)$ (M = Ni, Cu) and $M(TPPO)_2(SO_4)$ (M = Fe, Ni). Infrared spectra are given in Table II, and Figure 1; with the exception of the $CoSO_4$–LNO complex, the new complexes exhibit ir spectra devoid of coordinated water bands. In the case of the former complex, coordinated aquo groups are presumably strongly coordinated, as indicated by the fact that this complex was not dehydrated, even after prolonged desiccation over P_2O_5. Electronic spectral

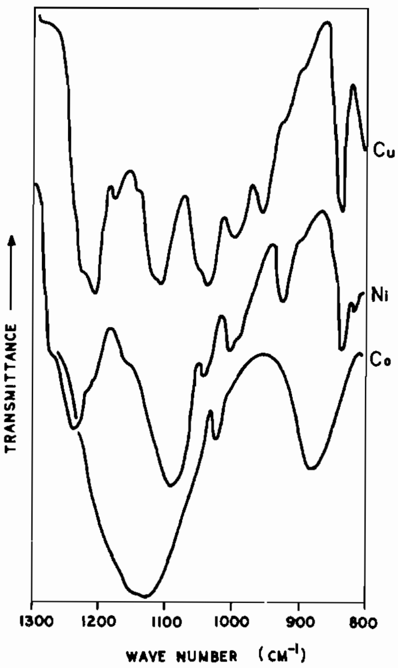


Figure 1. Infrared spectra (1300–800 cm^{-1}; Nujol mulls between IRTRAN 2 (ZnS) windows) of LNO complexes with Co(II), Ni(II) and Cu(II) sulfates.

and magnetic data are given in Table III. Most of the new complexes are insoluble in common organic solvents (*i.e.*, alcohols, ketones, aliphatic and aromatic chlorinated hydrocarbons, nitromethane, nitrobenzene, acetonitrile, *etc.*), the LNO complexes with $FeSO_4$ and $CuSO_4$ are sparingly soluble in nitromethane: $10^{-3}M$ nitromethane solutions of these complexes exhibit molar conductance values of 17 and 19 Ω^{-1} cm^2 mole^{-1}, respectively.

Discussion

Infrared Evidence

Coordination of the ligands through the N–O or P–O oxygen is demonstrated by the negative ν_{N-O} or ν_{P-O} frequency shifts[1,2,4,6-10] (Table II, Figure 1). In the spectra of the TPPO complexes, ν_{P-O} partially overlaps with the strong ligand absorption at 1122 cm^{-1};[11] both the Fe(II) and Ni(II) sulfate–TPPO complexes exhibit two absorption maxima in the 1121–1114 cm^{-1} region.

Distinction between ionic (T_d) and coordinated sulfate groups can be generally based on ir evidence.[12-20] The only new complex exhibiting ir bands attributable to the presence of ionic sulfate is Co(LNO)$(OH_2)_n(SO_4)$ (Table II, Figure 1). In the ir spectra of this complex the ν_3 and ν_4 modes of the SO_4 group

TABLE III. Electronic Spectra and Magnetic Moments (300° K) of Metal Sulfate Complexes with LNO and TPPO.

Complex	Electronic Spectra		Magnetic Susceptibilities	
	Medium	λ_{max}, nm (ε_{max})	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, BM
$[Fe(LNO)(SO_4)]_2$	Nujol $3.6 \times 10^{-3}M$ in CH_3NO_2	840s, 1142w, sh 930(7.7)	9998	4.94
$[Fe(TPPO)_2(SO_4)]_x$	Nujol	828m, sh, 987m, sh 1091m, sh	11029	5.15
$[Co(LNO)(OH_2)_n](SO_4)$	Nujol	460s, sh, 480s, sh, 540s, sh, 615m, sh, 860m, sh, 1200m, b	8695	4.59[a]
$[Ni(LNO)_2(SO_4)]_2$	Nujol	431s, sh, 500m, sh, 712m, sh, 1070w, b, sh	4535	3.32
$[Ni(TPPO)_2(SO_4)]_x$	Nujol	409s, sh, 496m, sh, 640m, sh, 1100w, vb	3958	3.10
$[Cu(LNO)_2(SO_4)]_2$	Nujol $3.5 \times 10^{-3}M$ in CH_3NO_2	695vs, 788vs, 839vs, 1090s, sh 738(25), 770sh(25), 968(15), 1180(9), 1250sh	1478	1.90

Abbreviations: s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.
[a] The μ_{eff} value of 4.59BM was calculated for the formula $[Co(LNO)(OH_2)_n](SO_4)$, where n = 4; for n = 5, μ_{eff} is 4.69BM($10^6\chi_g$ = 9157 cgsu).

appear as single, strong bands; ν_1 is weakly ir-active, while ν_2 is ir-inactive.[12] It should be noted that Ahuja interpreted similar spectral evidence for 1:1 complexes between $ZnSO_4$ and pyridine N-oxides as suggestive of highly polymeric structures, involving bridging sulfato ligands, coordinated through all the oxygen atoms of the sulfato group; under these conditions, the coordinated sulfato group might be expected to retain an essentially tetrahedral symmetry.[4] Nevertheless, Dubler and Oswald reported recently that $Co_3(OH)_2(SO_4)_2 \cdot 2H_2O$, a polynuclear complex, involving bridging sulfate, coordinated through all four SO_4 oxygens, exhibits splittings of the ν_3 and ν_4 SO_4 modes and a strongly ir-active $\nu_1(SO_4)$ mode, owing to considerable lowering of the T_d symmetry of the sulfato ligand.[19] It is, therefore, obvious that the sulfate group is ionic in the new $CoSO_4$–LNO complex. The coordinated water bands occur at 3200 (ν_{OH}) and 1630 (δ_{H-O-H}) cm^{-1} in this complex.

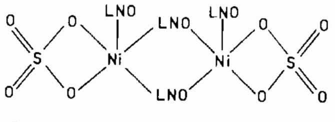
The rest of the new complexes reported contain exclusively coordinated sulfato ligands, as suggested by their ir spectra (Table II, Figure 1). The sulfato group may act either as a unidentate ligand with C_{3v} local site symmetry or as a bidentate ligand with C_{2v} symmetry.[12–20] In the latter case, it may act either as a chelating or as a bridging ligand.[12–20] Complexes involving monodentate sulfato ligands exhibit splittings of the ν_3 and ν_4 (SO_4) modes into two bands and ir-active ν_1 and ν_2 modes.[12,17] In bidentate bridging or chelating sulfato complexes, ν_3 and ν_4 are split into three bands, while ν_1 and ν_2 are again ir-active.[12–20] Distinction between chelating and bridging sulfato ligands can be based on the positions of the ν_3 bands; thus, complexes involving chelating bidentate sulfate exhibit the three ν_3 absorptions at 1240–1000 cm^{-1}, while those containing bridging bidentate sulfate show these bands at 1200–1030 cm^{-1}.[12–16,18,20] Examination of the spectra of the new complexes, in the light of the above knowledge, suggests that the Fe(II) and Ni(II) sulfate complexes with LNO probably involve chelating sulfato ligands, whereas the $CuSO_4$–LNO and MSO_4–TPPO (M = Fe, Ni) complexes contain bridging sulfato groups.

Tentative ν_{M-O} (ligand, aquo or sulfato) assignments are also given in Table II. For the $CoSO_4$–LNO complex, which does not involve coordinated sulfate, bands at 330–280 cm^{-1} were assigned as ν_{M-O}(LNO) and ν_{M-O}(aquo); the fact that the highest frequency metal-sensitive band in the spectrum of this complex occurs at 330 cm^{-1} is probably suggestive of coordination number six for the central Co(II) ion.[7] The rest of the complexes reported exhibit bands attributable to both ν_{M-O}(LNO or TPPO)[6–8,11] and ν_{M-O} (sulfato)[21,22] modes. These vibrational modes occur in the same region of the ir spectrum, and they would be expected to be strongly coupled; hence, they are presented together in Table II. Tentative assignments of primarily ν_{M-O} (ligand) and ν_{M-O} (sulfato) bands are made on the basis of the assumption that the former modes generally occur at somewhat higher wave numbers than the latter; this assumption is in agreement with ν_{M-O} (LNO or TPPO) and ν_{M-O} (sulfato) values reported in the literature.[6–8,11,21,22] The presence of two primarily ν_{M-O} (sulfato) bands ought to be expected, in view of the fact that the anion acts as a bi- or multi-dentate ligand in these complexes.[23] ν_{Cu-O} (LNO) occurs in the same frequency region as that reported for tetracoordinated Cu(II) complexes with this ligand,[7] while ν_{Ni-O} (LNO or TPPO) and ν_{Fe-O} (TPPO) appear in the region corresponding to reported ν_{M-O} values for pentacoordinated complexes of these metal ions with LNO and TPPO.[7,24] Two bands with the characteristics of ν_{M-O} (ligand) appear in the spectra of the $NiSO_4$–LNO and MSO_4–TPPO (M = Fe, Ni) complexes; this is probably suggestive of structures involving both terminal and bridging LNO or TPPO ligands.[6,7,25] ν_{Fe-O} (LNO) occurs at 371 cm^{-1} in Fe(LNO)(SO_4); in the square planar $[Fe(LNO)_4]^{2+}$ cationic complex ν_{Fe-O} occurs as a doublet at 402 and 380 cm^{-1}.[7]

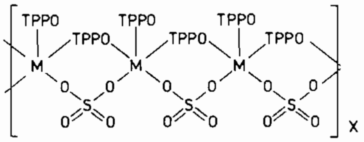
Electronic Spectra and Magnetic Moments

The electronic spectrum of the $CoSO_4$–LNO complex may be attributed to a distorted octahedral configuration[26] (Table III). The magnetic moment of this complex (4.59 or 4.69 BM; *cf.* Table III) is within the range of values reported for hexacoordinated Co(II) complexes with aromatic amine N-oxides,[26] while the low frequency ir spectral evidence also favors coordination number six for the central Co^{2+} ion (*vide supra*). Possible structures for this compound include: (a) a monomer of the type $[Co(LNO)(OH_2)_5]$ and (b) an LNO-bridged dimer of the type $[(H_2O)_4Co(LNO)_2Co(OH_2)_4](SO_4)_2$. In view of the insolubility of the complex in common organic solvents, the latter structure appears as more probable.

The electronic spectra and magnetic moments of the $NiSO_4$–LNO and MSO_4–TPPO (M = Fe, Ni) complexes may be attributed to pentacoordinated configurations,[6–8,24,27,28] which are also suggested by the positions of the ν_{M-O} (LNO) bands (*vide supra*). In the case of $Ni(LNO)_2(SO_4)$, which involves chelating sulfato ligands, a binuclear structure with both terminal and bridging LNO ligands is most probable (structure I).



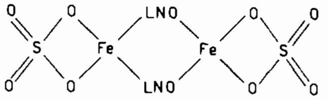
(I)



(II)

For the TPPO complexes, which contain bridging sulfato ligands and, most probably, both terminal and bridging TPPO groups, the polynuclear structure II would seem as the most compatible with the overall evidence.

The $CuSO_4$–LNO complex exhibits splittings of the d–d band; this does not necessarily exclude a tetracoordinated configuration, as suggested by the position of ν_{Cu-O} (LNO) (*vide supra*). In fact, $[Cu(PNO)_4](ClO_4)_2$, for example, which involves a square planar CuO_4 moiety,[29] reportedly shows splittings of the d–d transition.[30] A binuclear structure with bridging sulfato and terminal LNO ligands (*i.e.*, $[(LNO)_2Cu-(OS(O_2)O)_2-Cu(LNO)_2]$), involving square planar CuO_4 moieties, but an overall symmetry lower than D_{4h}, is the most probable for this complex. Finally, the $FeSO_4$–LNO complex is rather difficult to formulate. The fact that ν_{Fe-O} (LNO) is (as is also the case with ν_{Co-O} (LNO) in the $CoSO_4$ complex) considerably weaker than the corresponding ν_{M-O} bands in the Ni(II) and Cu(II) sulfate–LNO complexes, may imply the exclusive presence of bridging LNO ligands in the Fe(II) complex.[31] The binuclear structure III would appear as possible for this compound, whose electronic spectrum may be attributed to a tetracoordinated configuration.[7]



(III)

A higher polymeric structure, involving bridges between dimeric molecules of structure III, formed by coordination of one of the two uncoordinated oxygen atoms of the sulfato ligand in (III) to an Fe^{2+} ion of a neighboring dimer would also be compatible with the ir evidence.[20] Nevertheless, the solubility of the Fe(II) and Cu(II) sulfate–LNO complexes in some organic solvents (*cf.* experimental section) is in favor of mono- or bi- rather than poly-nuclear configurations for these compounds. The fact that the corresponding Ni(II) and Co(II) complexes with LNO are insoluble in common organic solvents does not necessarily suggest that these compounds are higher polymers, on the other hand. In fact, bi- or poly-nuclear Cu(II) halide complexes with pyridine N-oxides dissolve in a variety of organic solvents,[31,32] while their Mn(II), Ni(II) and Co(II) analogs exhibit considerable resistance to dissolution in organic media.[33]

A comment concerning the magnetic properties of the new complexes should also be made at this point. In fact, despite the fact that these compounds appear to be generally bi- or poly-nuclear, their magnetic moments are normal for high-spin complexes of the 3d metal ions under investigation. Bi- or poly-nuclear, N- or P-oxide-bridged Cu(II) complexes usually exhibit subnormal magnetic moments, attributable to spin–spin coupling occurring via a superexchange mechanism operating through the orbitals of the bridging oxygen atoms.[1,2,31,32,34] Nevertheless, the $CuSO_4$–LNO complex reported here appears to involve $Cu-(OS(O_2)O)_2-Cu$ rather than $Cu-(O)_2-Cu$ linkages. Superexchange through the –O–S–O-bridges would be rather unlikely, whilst demagnetization by direct Cu–Cu interaction is presumably impeded by the relatively long distance between the Cu(II) ions in the dimer.[35] As far as the new complexes with other 3d metal ions (*i.e.*, Fe(II), Co(II) and Ni(II)), it should be pointed out that several bi- or poly-nuclear Co(II) and Ni(II) halide complexes with aromatic amine N-oxides, reported in the literature, exhibit normal paramagnetism for high-spin compounds of these metal ions.[33,36]

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