Contribution from the School of Chemistry, University of New South Wales, Kensington, N.S.W., 2033, Australia

Metal Chelates of α-Diimines Containing a Benzothiazole Moiety. III. Infrared, Thermogravimetric, and Magnetic Investigations of Some Sulphate Complexes

P. S. K. Chia, L. F. Lindoy, and S. E. Livingstone

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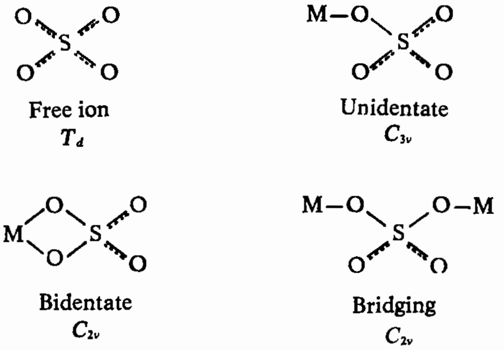
Some metal sulphate complexes of the α-diimine ligands, 2-(2-pyridyl)benzothiazole (pbt) and 2-(6-methyl-2-pyridyl)benzothiazole (mpbt) are reported. Their infrared spectra indicate that the complexes can be divided into three types: (i) the complexes $[Co\,pbt(H_2O)_4]SO_4$, $[Ni\,pbt(H_2O)_4]SO_4 \cdot \frac{1}{2}H_2O$, $[Cd\,pbt(H_2O)_2]SO_4$, *and* $[Cd\,mpbt(H_2O)_2]SO_4$ *which contain ionic sulphate; (ii) the complex* $[Pd\,pbt\,SO_4(H_2O)]$ *in which the sulphato group behaves as a unidentate ligand; (iii) the complexes* $Pd\,mpbt\,SO_4$, $Ni\,pbt\,SO_4$, $Cu\,pbt(H_2O)_2SO_4$, $Cu\,pbt\,py_2SO_4$, *and* $Cu\,mpbt(H_2O)_2SO_4$, *which contain bridging sulphato groups. The magnetic moments of* $Cu\,pbt(H_2O)_2SO_4$ *and* $Cu\,mpbt(H_2O)_2SO_4$ *are constant over the temperature range 300-80°K, indicating the absence of any anti-ferromagnetic interaction in these compounds.*

Introduction

Metal complexes may contain the sulphate radicle as a free ion or as a coordinated group. In the latter case the sulphate radicle may function as a unidentate, bidentate, or bridging ligand. Nakamoto *et al.*[1,2] have discussed the differences in the infrared spectra of compounds containing the various types of sulphate linkage. The SO_4^{2-} ion belongs to the symmetry point group T_d and only the vibrations ν_3 and ν_4 are infrared active and occur as strong bands at *ca.* 1100 and 610 cm^{-1}, respectively. The symmetry of the sulphate ion is lowered on coordination, as shown in Figure 1. The change in selection rules and the removal of degeneracy are given in Table I.[1]


Free ion T_d

Unidentate C_{3v}

Bidentate C_{2v}

Bridging C_{2v}

Figure 1. Types of linkage for the sulphate ion in metal complexes.

Other investigators have examined the infrared spectra of metal sulphates and sulphato complexes and they have used Nakamoto's criteria to ascertain the type of linkage present.[3-11]

In previous parts of this series[12,13] we have reported various metal chelates of two α-diimine ligands, 2-(2-pyridyl)benzothiazole (pbt; I, R=H) and 2-(6-methyl-

Table I. Correlation Table for T_d, C_{3v}, and C_{2v}

Point group	ν_1 symmetric stretch	ν_2 symmetric bend	ν_3 asymmetric stretch	ν_4 asymmetric bend
T_d	A_1 (R)	E (R)	T_2 (I, R)	T_2 (I, R)
C_{3v}	A_1 (I, R)	E (I, R)	A_1 (I, R)+E (I, R)	A_1 (I, R)+E (I, R)
C_{2v}	A_1 (I, R)	A_1 (I, R)+A_2 (R)	A_1 (I, R)+B_1 (I, R)+B_2 (I, R)	A_1 (I, R)+B_1 (I, R)+B_2 (I, R)

I=Infrared active; R=Raman active.

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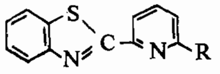
2-pyridyl)benzothiazole (mpbt; I, R=CH_3). We now report some sulphate complexes of these two ligands.



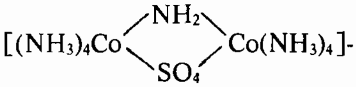
(I)

Results and Discussion

Some metal complexes containing sulphate have been obtained with the α-diimines pbt (I; R=H) and mpbt (I; R=CH_3) by the reaction of the benzothiazole with the metal sulphate in aqueous alcohol. The complexes are listed in Table II, together with their infrared spectral bands which are considered to arise from vibrational modes of the sulphate radicle. Since the infrared spectra of the ligands pbt and mpbt display several bands of medium intensity in the regions 1300-900 cm^{-1} and 650-400 cm^{-1}, assignment of the sulphate bands was made only after reference to the spectra of some metal complexes of these ligands which do not contain sulphate.

The complexes $[Co\,pbt(H_2O)_4]SO_4$ and $[Ni\,pbt(H_2O)_4]SO_4 . \frac{1}{2}H_2O$ have been previously reported and were assigned octahedral structures on the basis of their visible reflectance spectra and magnetic moments.[12] The infrared spectra of these two complexes and of the cadmium complexes $Cd\,pbt(H_2O)_2SO_4$ and $Cd\,mpbt(H_2O)_2SO_4$ display ν_3 of the sulphate group as a single broad band at *ca.* 1100 cm^{-1} and ν_4 at *ca.* 600 cm^{-1}. No definite absorptions attributable to ν_1 and ν_2 appear. These data indicate that the sulphate groups have T_d symmetry and consequently are ionic. For the cobalt and nickel atoms to have an octahedral configuration in these complexes four water molecules must be coordinated. Similarly the two water molecules must be coordinated in both cadmium complexes for the cadmium atom to be quadricovalent. Thermogravimetric analyses show that the cobalt, nickel, and cadmium complexes quantitatively lose their water content when heated to 200°.

In the spectrum of $Pd\,pbt\,SO_4H_2O$ ν_3 splits into two strong bands at 1145 and 1031 cm^{-1}, indicating C_{3v} symmetry. This spectrum is similar to those of $[Pd(NH_3)_2SO_4H_2O]$ and $[Co(NH_3)_5SO_4]Br$, which contain unidentate sulphato groups. The former displays ν_3 as two bands at 1140-1110 and 1050-1030 cm^{-1},[7] while the latter displays ν_3 at 1143-1117 and 1044-1032 cm^{-1}, ν_1 at 970 cm^{-1}, ν_2 at 438 cm^{-1}, and ν_4 at 645 and 604 cm^{-1}.[1] Accordingly the complex $Pd\,pbt\,SO_4H_2O$ is considered to contain a unidentate sulphato group and a coordinated water molecule

On the other hand the spectrum of $Pd\,mpbt\,SO_4$ shows ν_3 at 1187, 1140, and 1023 cm^{-1} and ν_4 at 665, 619, and 560 cm^{-1}. This splitting of ν_3 and ν_4 into three bands indicates C_{2v} symmetry and hence the sulphato group is behaving as a chelating or a bridging ligand in this complex. The spectrum of $Pd(NH_3)_2SO_4$, which contains a bridging sulphato group, displays ν_3 as three bands at 1195, 1110, and 1035 cm^{-1},[7] while the spectrum of  $[(NH_3)_4Co\overset{NH_2}{\underset{SO_4}{\diamond}}Co(NH_3)_4](NO_3)_3$ displays ν_3 at 1170, 1105, and 1055 cm^{-1} and ν_4 at 641, 610, and 571 cm^{-1}.[1] Eskenazi *et al.*[7] observed that the highest frequency band occurs well above 1200 cm^{-1} in complexes containing a chelating sulphato group and below 1200 cm^{-1} in sulphato-bridged complexes. Consequently the complex $Pd\,mpbt\,SO_4$ is considered to possess either a dimeric or a polymeric structure involving sulphato bridges, so that each palladium atom is linked to two nitrogen and two oxygen atoms.

The spectra of $Ni\,pbt\,SO_4$, $Cu\,pbt(H_2O)_2SO_4$, $Cu\,pbt\,py_2SO_4$, and $Cu\,mpbt(H_2O)_2SO_4$ indicate that the sulphato group is bridging in these complexes also

Table II. Sulphate Complexes and Their Infrared Bands (cm^{-1})

Compound	Colour	ν(OH)	Sulphate bands				Proposed coordination of sulphate ion
			ν_1	ν_2	ν_3	ν_4	
$[Co\,pbt(H_2O)_4]SO_4$	orange	3200 b	—	—	1070 sb	600 m	Ionic
$[Ni\,pbt(H_2O)_4]SO_4 . \frac{1}{2}H_2O$	bluish-green	3200 b	—	—	1070 sb	595 w	Ionic
$[Cd\,pbt(H_2O)_2]SO_4$	colourless	3100 b	—	—	1105 sb	599 s	Ionic
$[Cd\,mpbt(H_2O)_2]SO_4$	colourless	3060 b	—	—	1100 sb	626 m	Ionic
$Pd\,pbt\,SO_4H_2O$	yellow	3460 b	937 s	432 m	1145 s 1031 s	[a] 605 m	Unidentate
$Pd\,mpbt\,SO_4$	yellow	—	960 w	428 m	1187 m 1140 s 1023 m	665 s 619 m 560 s	Bridging
$Ni\,pbt\,SO_4$	green	—	[a]	427 m	1145 s 1110 s 1075 sh	641 m 604 sh 586 s	Bridging
$Cu\,pbt(H_2O)_2SO_4$	bluish-green	3100 b	[a]	429 w	1157 s 1093 s 1060 m	650 m 595 sh 605 sh	Bridging
$Cu\,pbt\,py_2SO_4$	dark blue	—	[a]	430 m	1157 s 1095 m 1050 s	642 m 605 w 585 w	Bridging
$Cu\,mpbt(H_2O)_2SO_4$	bluish-green	3000 b	975 m	428 m	1147 s 1112 s 1038 s	625 sh 612 s	Bridging

[a] Obscured by ligand absorption. s, strong; m, medium; w, weak; b, broad; sh, shoulder.

(see Table 2). The infrared spectrum of Cu pbt-$(H_2O)_2SO_4$ in the region of ν_3 is shown in Figure 2.

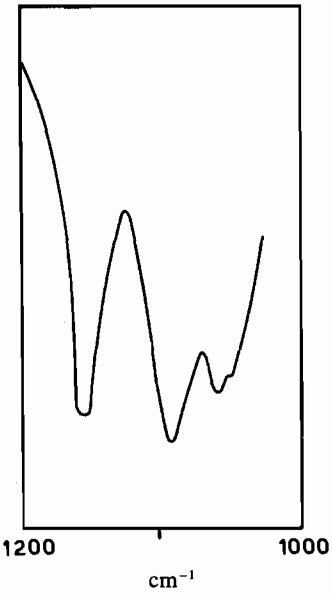


Figure 2. Infrared spectrum of Cu pbt$(H_2O)_2SO_4$ in the region 1200-1000 cm^{-1} showing the splitting of ν_3.

The compound Ni pbt SO_4 was obtained by heating of the hydrated complex [Ni pbt$(H_2O)_4$]SO_4. ½H_2O. It readily takes up water and because of its hygroscopic nature it was not investigated further.

The complexes Cu(chelate)$(H_2O)_2SO_4$ (chelate = 2,2′-bipyridyl or 8-methylthioquinoline) have also been assigned sulphato-bridged structures.[5,8] The visible reflectance spectra of Cu pbt$(H_2O)_2SO_4$ and Cu mpbt-$(H_2O)_2SO_4$ display a very broad absorption band cèntred at 13800 cm^{-1} (725 mμ) and 13150 cm^{-1} (760 mμ), respectively. These spectra are indicative of six-coordinate copper(II).[14,15] The water is lost quantitatively when the complexes are heated to 180°. The anhydrous compounds are extremely hygroscopic and readily revert to the diaqua complexes in moist air. If the anhydrous compound Cu pbt SO_4 is allowed to stand in an atmosphere of pyridine, it absorbs pyridine to yield the dark blue complex Cu pbt py_2SO_4, which loses its pyridine quantitatively when heated to 180° on the thermogravimetric balance. The infrared spectrum of the dipyridine complex is very similar to that of the diaqua complex. It is apparent that pyridine and water are coordinated in these comlpexes so that the copper atom achieves six-coordination by being surrounded by the two nitrogen atoms of the α-diimine, two water or pyridine molecules, and two oxygen atoms from bridging sulphato groups in either a dimeric or polymeric structure.

The magnetic susceptibilities of Cu pbt$(H_2O)_2SO_4$ and Cu mpbt$(H_2O)_2SO_4$ were measured over the temperature range 300-80°K. The magnetic data are given in Table III and the Curie-Weiss plot for the latter compound is shown in Figure 3. Both complexes obey the Curie-Weiss Law $\left(\chi'_M = \frac{C}{T-\theta}\right)$. The low values for θ, –5° for Cu pbt$(H_2O)_2SO_4$ and –6° for Cu mpbt$(H_2O)_2SO_4$, exclude the possibility of antiferromagnetic interaction.

Table III. Magnetic Data for Copper Complexes

T°K	$10^6\chi'_M$	$1/\chi'_M$	μ (B.M.)
	Cu pbt$(H_2O)_2SO_4$		
291	1590	628.9	1.93
263	1770	565.0	1.94
233	2020	494.8	1.95
203	2300	434.4	1.94
173	2690	371.7	1.94
143	3200	312.5	1.92
113	3990	250.6	1.91
93	4710	212.3	1.88
80	5300	188.7	1.85
	Cu mpbt$(H_2O)_2SO_4$		
T°K	$10^6\chi'_M$	$1/\chi'_M$	μ (B.M.)
298	1462	684.0	1.87
273	1607	622.3	1.88
243	1834	545.2	1.90
213	2104	475.3	1.90
183	2445	409.0	1.90
133	3340	299.4	1.89
83	5180	193.0	1.86

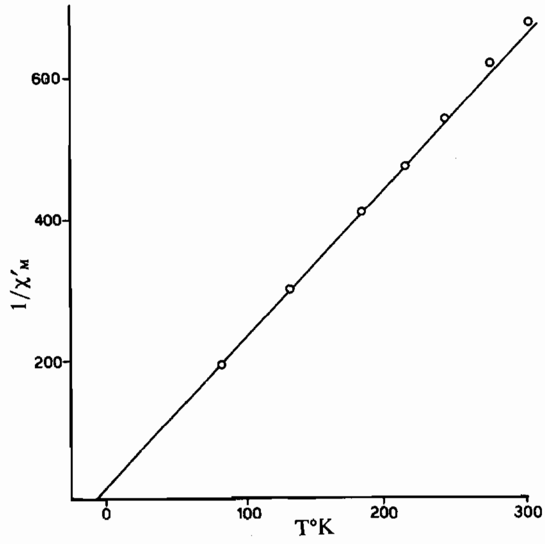


Figure 3. Curie-Weiss plot for Cu mpbt$(H_2O)_2SO_4$.

Experimental Section

Analyses. Analyses for carbon, hydrogen, and nitrogen were acrried out by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales. Sulhpur was determined by the Australian Microanalytical Service, Melbourne.

Physical Measurements. The infrared spectra were obtained from Nujol or halocarbon mulls on a Perkin-

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Elmer 337 spectrophotometer. The diffuse reflectance spectra were measured on a Zeiss PMQ II spectrophotometer with magnesium oxide as the reference. The thermogravimetric measurements were made on a Stanton Thermobalance, model TR-01. The magnetic susceptibilities were determined on a Newport Variable Temperature Gouy balance.

2-(2-Pyridyl)benzothiazole. The preparation of this compound has been reported previously.[16,17]

2-(6-Methyl-2-pyridyl)benzothiazole. The preparation of this compound has been described in the previous Part of this series.[13]

Preparation of the Metal Complexes. The complexes were prepared by the same general method. A solution of the benzothiazole (2 mmoles) in alcohol (50 ml) was added slowly to a hot solution of the metal sulphate (2 mmoles) in water (20 ml). The mixture was heated for 5 min, whereupon the complex was filtered off, washed with alcohol, and dried *in vacuo* over phosphoric oxide. For the preparation of the palladium complexes acetone was used in place of alcohol and the reaction was carried out at room temperature.

Diaqua-2-(2-pyridyl)benzothiazolecadmium(II) Sulphate. Anal. Calcd. for $C_{12}H_{12}CdN_2O_6S_2$: C, 31.6; H, 2.6; N, 6.1; S, 14.0; H_2O, 7.9%. Found: C, 32.0; H, 2.9; N, 5.9; S, 14.1; loss on heating to 200°, 7.7.

Diaqua-2-(6-methyl-2-pyridyl)benzothiazolecadmium(II) Sulphate. Anal. Calcd. for $C_{13}H_{14}CdN_2O_6S_2$: C, 33.2; H, 3.0; Cd, 23.9; S, 13.6; H_2O, 7.7%. Found: C, 33.0; H, 3.0; Cd, 23.6; S, 13.6; loss on heating to 200°, 7.4.

Sulphatoaqua-2-(2-pyridyl)benzothiazolepalladium(II). Anal. Calcd. for $C_{12}H_{10}N_2O_5PdS_2$: C, 33.3; H, 2.3; N, 6.5; S, 14.8%. Found: C, 33.5; H, 2.6; N, 6.2; S, 14.7.

Sulphato-2-(6-methyl-2-pyridyl)benzothiazolepalladium(II). Anal. Calcd. for $C_{13}H_{10}N_2O_4PdS_2$: C, 36.4; H, 2.4; N, 6.5; Pd, 24.2%. Found: C, 35.9; H, 2.9; N, 6.1; Pd, 24.2.

Sulphatodiaqua-2-(2-pyridyl)benzothiazolecopper(II). Anal. Calcd. for $C_{12}H_{12}CuN_2O_6S_2$: C, 35.3; H, 3.0; N, 6.9; S, 15.7; H_2O, 8.8%. Found: C, 35.0; H, 3.2; N, 6.5; S, 15.3; loss on heating to 200°, 8.5.

Sulphatodiaqua-2-(6-methyl-2-pyridyl)benzothiazolecopper(II). Anal. Calcd. for $C_{13}H_{14}CuN_2O_6S_2$: C, 37.0; H, 3.3; Cu, 15.1; H_2O, 8.5%. Found: C, 37.0; H, 3.3; Cu, 15.2; loss on heating to 200°, 8.1.

Sulphato-2-(2-pyridyl)benzothiazolenickel(II). Tetraaqua-2-(2-pyridyl)benzothiazolenickel(II) sulphate demihydrate was heated at 200° for 20 min to give the anhydrous complex (Found: loss on heating, 18.3. Calcd. loss of $4.5H_2O$, 18.1%).

Sulphatobispyridine-2-(2-pyridyl)benzothiazolecopper(II). Sulphatodiaqua-2-(2-pyridyl)-benzothiazolecopper(II) was heated to 180°. The resulting anhydrous compound was allowed to stand in an atmosphere of pyridine for 24 hrs, where upon the pyridine complex was obtained (Calcd. for $C_{22}H_{18}CuN_4O_4S_2$: C, 49.8; H, 3.4; Cu, 12.0; N, 10.6; pyridine, 43.0%. Found: C, 48.9; H, 4.0; Cu, 12.4; N, 10.2; loss on heating at 180°, 43.0).

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