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Syntheses and coordination studies of 2-(diphenylphosphinomethyl)pyridine *N*,*P* dioxide with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} tetrafluoroborate

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ABSTRACT

Several new coordination complexes of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} were synthesized by the reaction of their corresponding tetrafluoroborate salts with 2-(diphenylphosphinomethyl)pyridine *N*,*P* dioxide, **L**. All structures were determined by single-crystal X-ray crystallography showing an octahedral environment around the metal centers. Single crystals of $M(BF_4)_2L_2(S)_2$ (M = Co^{2+}, Ni^{2+} or Zn^{2+}; S = MeOH or CH_3CN) were obtained at −5 °C by slow diffusion of ether into solutions of these complexes. When these crystals were re-dissolved in methanol and allowed to grow again at room temperature using the same technique and solvent system, the product obtained presented a 3:1 ratio ligand-to-metal. The complex $[Cu(BF_4)_2L_2(MeOH)](BF_4)$, exhibits two units of **L**, one molecule of MeOH and one counter-anion coordinated to the Cu^{2+} center. This can be attributed to the steric restrictions generated by the lower symmetry in this complex, a product of significant Jahn–Teller effects, which favors a long range interaction between the metal center and a less coordinative counter-anion, compared to a MeOH unit. A 1:1 ligand-to-metal ratio complex of Ni^{2+} was also obtained by allowing the starting materials to react for only a short time. Attempts to obtain single crystal of complexes of Co^{2+}, Cu^{2+} or Zn^{2+} in a 1:1 ratio were not successful. The resulting 3:1 ligand-to-metal products were fully characterized by elemental analysis, UV–Vis spectroscopy and FT-IR spectroscopy.

1. Introduction

Chelating ligands and their coordination behavior have been studied since the inception of coordination chemistry. They have received great attention due to their ability to coordinate to transition metals, an important characteristic in many biological processes and industrial applications. They have been used in metal ion extraction [1–5], synthesis of new luminescent and polymeric materials and homogeneous catalysis, treatment of human diseases related to metal overload (e.g. Hemochromatosis [6–8], saturnism [9,10], aluminum overload [11,12]), among others [13–20].

It is known that anionic or neutral ligands with strong oxygen donor centers form stable coordination complexes with hard acids. For example, chelating phosphine oxides have been used in the synthesis of new luminescent materials due to their capability of stabilizing metal centers with higher oxidation state [21]. Also, they possess an enhanced capacity to improve both photoluminescent and electroluminescent properties of these complexes through the reduction of solvent-induced quenching and improvement of intramolecular electron transfer [22]. These ligands have also been shown to be good extractants for lanthanide and actinide ions under specific conditions [23,24]. Recently, Rosario-Amorin described the synthesis of monofunctional P=O-containing ligands and their coordination properties towards several f-block metal cations. In this study they showed that these ligands could be used for liquid–liquid solvent extraction of hard acceptor ions [25].

The design of compounds based on *N*-oxides has been of interest due to their dual application in both metal-free catalytic transformations and as ligands in metal-based catalysis [26]. Liang synthesized different monofunctional ligands containing N–O groups and investigated their role in the Cu-catalyzed *N*-arylation of imidazoles using water as a solvent. They found that ligands based on pyridine *N*-oxides were more beneficial to the catalytic process than their pyridine analogs. The higher catalytic activities obtained were partly attributed to their excellent solubility in water, and out of three different N–O-containing ligands employed, the bidentate with the greatest flexibility gave the highest yield [27]. In 2009, Zhang developed a novel chiral indium complex, based on (*S*)-pipecolic acid-derived *N*,*N*′-dioxide ligands, for the enantioselective allylation of ketones. Their results showed that the novel chiral indium complex could be an efficient catalyst for this reaction yielding good enantioselectivity. In a more recent work, Liu synthesized a new family of C_2-symmetric *N*,*N*′-dioxide

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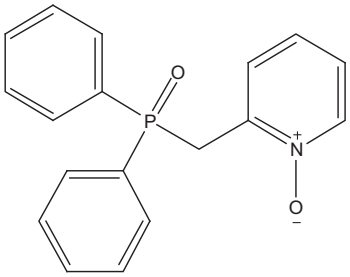

Scheme 1. Structure of 2-(diphenylphosphinomethyl)pyridine *N,P* dioxide (**1**).

amide ligands and demonstrated that these compounds could participate in a wide range of chiral ligand–metal-catalyzed and organocatalyzed asymmetric reactions under mild reaction conditions obtaining excellent enantioselectivity and activity [28].

Siddall suggested that bifunctional carbamoylmethylphosphonate ligands with the ability to adopt bidentate chelate structures in solution could be used as improved chelating agents for the recovery of lanthanide and actinide ions, when compared to the monofunctional organophosphoryl and organoamide ligands [29]. Several studies on the coordination chemistry of bifunctional ligands that contain both P=O and N–O donors have demonstrated that these chelating reagents produce stable complexes with 3d

Table 1
Crystallographic data for compounds **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{54}H_{48}B_2CoF_8N_3O_6P_3$	$C_{54}H_{48}B_2F_8N_3NiO_6P_3$	$C_{54}H_{48}B_2CuF_8N_3O_6P_3$	$C_{54}H_{48}B_2F_8N_3O_6P_3Zn$
Formula mass	1160.41	1192.24	1202.38	1198.90
a (Å)	13.9051(9)	10.5814(19)	14.1007(10)	10.5390(5)
b (Å)	23.1098(16)	15.021(2)	22.6498(17)	15.0341(7)
c (Å)	17.9489(11)	17.249(3)	17.5725(12)	17.2991(8)
α (°)	90	90	90	90
β (°)	95.906(3)	91.786(6)	98.585(4)	92.116(2)
γ (°)	90	90	90	90
V (Å^3)	5737.2(6)	2740.3(7)	5549.4(7)	2739.1(2)
Z	4	2	4	2
Crystal System	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*P*2(1)/*c*	*P*2(1)	*P*2(1)/*c*	*P*2(1)
T (K)	110(2)	110(2)	110(2)	110(2)
D_{calc} (g/cm^3)	1.343	1.445	1.439	1.454
μ (mm^{-1})	0.458	0.524	0.562	0.618
$2\theta_{maz}$ (°)	28.31	26.75	28.35	27.72
Reflections measured	103376	27498	50561	41116
Reflections used	14240	10845	13836	12760
Data/restraints/parameters	14240/0/732	10845/1/714	13836/4/738	12760/1/714
R_1 [$I > 2\sigma(I)$]	0.0444	0.0582	0.0539	0.0438
wR_2 [$I > 2\sigma(I)$]	0.1029	0.1392	0.1163	0.1041
R (F^2_o) (all data)	0.0611	0.0701	0.1020	0.0535
R_w (F^2_o) (all data)	0.1104	0.1460	0.1419	0.1108
Goodness-of-fit (GOF) on F^2	1.078	1.043	1.008	1.023

Table 2
Crystallographic data for compounds **5**–**9**.

	5	**6**	**7**	**8**	**9**
Empirical formula	$C_{44}H_{44}B_2CoF_8N_6O_4P_2$	$C_{39}H_{44}BF_4N_2NiO_7P_2$	$C_{37}H_{36}B_2CuF_8N_2O_5P_2$	$C_{39}H_{44}BF_4N_2O_7P_2Zn$	$C_{28}H_{31}B_2F_8N_6NiO_2P$
Formula mass	1015.34	860.22	887.78	866.88	746.89
a (Å)	17.7024(19)	13.175(5)	10.844(3)	13.245(9)	11.0974(5)
b (Å)	18.9467(17)	13.669(5)	12.839(4)	13.670(10)	25.2713(11)
c (Å)	14.0724(15)	14.543(4)	15.666(5)	14.573(10)	12.0411(6)
α (°)	90	67.989(7)	90.874(4)	67.655(13)	90
β (°)	90	69.059(11)	107.544(4)	68.811(11)	97.489(2)
γ (°)	90	77.423(7)	113.885(4)	77.101(14)	90
V (Å^3)	4719.9(8)	2257.1(13)	1877.9(10)	2264(3)	3348.1(3)
Z	4	2	2	2	4
Crystal System	orthorhombic	triclinic	triclinic	triclinic	monoclinic
Space group	*Pbcn*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*P*21/*n*
T (K)	110(2)	110(2)	110(2)	110(2)	110(2)
D_{calc} (g/cm^3)	1.429	1.266	1.570	1.272	1.482
μ (mm^{-1})	0.512	0.562	0.753	0.674	0.708
$2\theta_{maz}$ (°)	26.44	25.74	28.42	25.00	29.57
Reflections measured	37923	41663	18227	17372	37197
Reflections used	4857	8273	8720	7792	9298
Data/restraints/parameters	4857/0/305	8273/0/514	8720/0/519	7792/1/517	9298/0/438
R_1 [$I > 2\sigma(I)$]	0.0515	0.0756	0.0399	0.0805	0.0384
wR_2 [$I > 2\sigma(I)$]	0.1218	0.1977	0.0938	0.2193	0.0881
R (F^2_o) (all data)	0.0643	0.0916	0.0515	0.0974	0.0543
R_w (F^2_o) (all data)	0.1316	0.2059	0.1023	0.2286	0.0966
Goodness-of-fit (GOF) on F^2	1.033	1.041	1.034	1.048	1.023