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Syntheses, Structures and Physico-Chemical Properties of 2-Mercaptopyridine *N*-Oxide (Hmpo) Chelated Co- and Ni-Complexes with Phosphine Mediation

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2-Mercaptopyridine *N*-oxide (Hmpo) chelated complexes $[Co(mpo)_2\{P(OMe)_3\}_2]PF_6$ (**1**), $[Co(mpo)_3]\cdot{}^nBu_4NPF_6$ (**2**), [Ni(mpo)(dppe)]Cl·0.5H_2O·MeOH (**3**) and $[Ni(mpo)_2]\cdot{}^nBu_4NPF_6$ (**4**) were synthesized and their crystal structures characterized. The octahedral Co in **1** and **2** and the square planar Ni in **3** and **4** are chelated by mpo^-, while phosphite or diphosphine coordinated in *cis*-orientation in **1** and **3**, respectively. The co-crystallized salt $^nBu_4NPF_6$ in **2** and **4** extrude any solvent molecules that might form hydrogen bonds within the crystal lattices.

Key words: 2-mercaptopyridine *N*-oxide, trimethyl phosphite, diphenylphosphinoethane, CV measurement, crystal structure, Co and Ni complexes, voltammetry

The wide interest in the coordination chemistry of thiolato transition metal complexes follows from the fact that many biologically significant materials, such as enzymes and proteins contain M–S bonds at the active center, where M is usually an element of the first transition period [1]. Studies on cobalt complexes with mixed thiolate and phosphine ligands were initiated as early as thirty years ago due to their interesting spectroscopic, magnetic and eletronic properties. In the nineties, numerous cobalt complexes with combinations of mono-, bi- or tridentate phosphine and thiolato ligands have been identified structurally. The structures of nickel complexes were less versatile, only some mono- and dinuclear complexes were reported. In our past studies on thiolato ligands, 1,2-bidentate bivalent anions exhibit interesting and versatile coordination modes [2]. It is our interest now to study the behavior of univalent 1,2-bidentate ligands and also to investigate the effect of phosphorus containing ligands (phosphine or phosphite) on the chelating property of such ligands. 2-Mercaptopyridine *N*-oxide (Hmpo) is a convenient choice with most of its complexes so far reported mononuclear [3,4], where the only exception is complex $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br\cdot 2DMF$ containing actually mononuclear $Co(mpo)_2$ as building blocks [5]. Hereby we report two sets of complexes, in which replacement reactions oc-

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curred when different amount of Hmpo is present in solutions, showing the varied ligation ability of the phosphorus- and sulfur-containing ligands.

EXPERIMENTAL

Materials: Anhydrous $CoCl_2$, $NiCl_2$, $P(OMe)_3$, Nampo (sodium *2*-mercaptopyridine *N*-oxide), dppe (diphenylphosphinoethane), and $^nBu_4NPF_6$ were all from Aldrich and used as obtained. Solvent MeOH was first dried over 4 Å molecular sieves, and then distilled over Mg and I_2 and kept under N_2 for use. MeCN used in electrochemical studies was also dried carefully and distilled before use.

Measurements: Elemental analyses were performed on a Perkin-Elmer 240C analytical instrument. IR spectra were recorded on a Nicolet FTIR-5D spectrophotometer in KBr pellets. Cyclic voltammetric studies were performed on a HDV-7C potentiostat equipped with a DED-3 frequency generator and a 3086 X-Y recorder in a three-electrode cell with platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. $^nBu_4NBF_4$ was used as supporting electrolyte and scan rate was 100 mV/s. FABMS spectrum was obtained on a VG ZAB-HS instrument with *m*-nitrobenzyl alcohol as the matrix.

Preparation of complexes 1–4: All reactions were performed anaerobically under a nitrogen atmosphere in Schlenk type apparatus.

$[Co(mpo)_2\{P(OMe)_3\}_2]PF_6$ (1). To the MeOH solution (25 cm^3) of $P(OMe)_3$ (0.6 cm^3, 4.0 mmol), under stirring at room temperature, was added first the anhydrous $CoCl_2$ (0.13 g, 1.0 mmol), then Nampo (0.15 g, 1.0 mmol). The solution was stirred for 30 min and filtered, solvent was evaporated under reduced pressure to 15 cm^3 and $^nBu_4NPF_6$ (1.12 g, 1.0 mmol) was added. Dark red rod-like crystals of **1** crystallized when the filtrate was kept at 5°C for several days, yield 55%.

$[Co(mpo)_3]\cdot{}^nBu_4NPF_6$ (2). The same reaction process was applied as above, except that 2.0 mmol (0.30 g) of Nampo was added instead of 1.0 mmol. After several days in the ice-box, the reaction filtrate gave black block crystals of **2**, yield 50 %.

$[Ni(mpo)(dppe)]Cl\cdot 0.5H_2O\cdot MeOH$ (3). To the 25 cm^3 solution of dppe (0.40 g, 1.0 mmol) in MeOH was added first the anhydrous $NiCl_2$ (0.13 g, 1.0 mmol) with stirring at room temperature, then Nampo (0.15 g, 1.0 mmol). After stirring for 30 min., the solution was reduced in volume to 15 cm^3 and left at 5°C for several days to give black cubic crystals of **3**, yield 50 %.

$[Ni(mpo)_2]\cdot{}^nBu_4NPF_6$ (4). The same reaction process was employed as above, except that 2.0 mmol (0.3 g) of Nampo was added instead of 1.0 mmol. Besides, 1.0 mmol (1.12 g) of $^nBu_4NPF_6$ was added also and then the solution was left in the ice-box for several days to give black rod-like crystals of **4**, yield 40%.

Elemental analyses confirmed the compositions indicated.

Crystallographic studies: Single crystals of **1–4** of suitable size were selected directly from the reaction solutions and mounted on glass fibres and the intensity data were collected on a Siemens R3M X-ray diffractometer with graphite monochromated MoKα ($\lambda = 0.71073$ Å) radiation at 293 K in the ω-2θ scan mode and corrected for anisotropic decay, LP factors and absorptions empirically. The structures were solved by direct methods and refined on F^2 by full-matrix least squares method using Siemens SHELXTL-PC program package. All non-hydrogen atoms were refined anisotropically from the difference Fourier map, while the hydrogen atoms were only added to the structural factor calculations isotropically but not refined. Crystallographic data are listed in Table 1.*

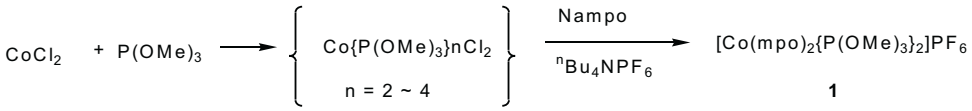
* Crystallographic data have been deposited with the Cambridge Crtystallographic Data Center as deposition no. 158442–158445 for complexes **1**–**4**, respectively.

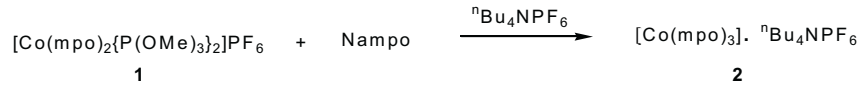
Table 1. Crystallographic data and data collection parameters for the complexes **1**–**4**.

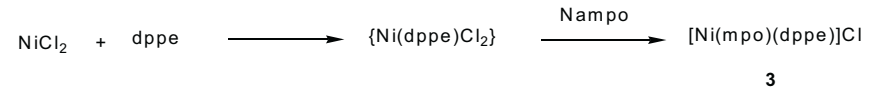
	1	**2**	**3**	**4**
Empirical formula	$C_{16}H_{26}N_2O_8S_2P_3F_6Co$	$C_{31}H_{48}N_4O_3S_3PF_6Co$	$C_{32}H_{33}ClNO_{2.5}P_2SNi$	$C_{26}H_{44}F_6N_3O_2S_2PNi$
Formula weight	529.25	824.81	659.75	698.44
Crystal system	Tetragonal	Orthorhombic	Monoclinic	Monoclinic
Space group	$P4_2/n$	$P2_1/1$	$P2_1/n$	$P2_1/c$
a, (Å)	19.039(7)	10.6850(10)	9.108(6)	10.542(5)
b, (Å)	19.039(7)	17.2690(10)	14.704(9)	17.758(9)
c, (Å)	15.170(10)	20.9470(10)	24.45(3)	17.43(2)
β, (°)	90	90	91.60	96.05
Volume (Å^3)	5499(5)	3865.1(5)	3273(5)	3244(5)
Z	10	4	2	4
ρ_{calc} (g cm^{-3})	1.598	1.417	1.339	1.430
μ (mm^{-1})	1.019	0.713	0.866	0.839
F (000)	2682	1720	1372	1464
Crystal size (mm^3)	0.40 × 0.30 × 0.36	0.40 × 0.34 × 0.30	0.45 × 0.40 × 0.32	0.42 × 0.45 × 0.30
θ range (deg)	2.02 to 24.99°	1.53 to 25.97°	2.17 to 22.51	2.26 to 25.00
Independent reflections	3035 (R_{int} = 0.0356)	4230 (R_{int} = 0.0000)	4226 (R_{int} = 0.1047)	5712 (R_{int} = 0.0631)
Max. and min. transmission	0.748 and 0.760	0.722 and 0.692	0.763 and 0.844	0.702 and 0.654
No. of variables	346	442	371	371
Goodness-of-fit on F^2	0.986	1.037	1.096	1.023
Final *R* indices ($I > 2\sigma(I)$)	R_1 = 0.0799 wR_2 = 0.2065	R_1 = 0.0814 wR_2 = 0.1983	R_1 = 0.1087 wR_2 = 0.2839	R_1 = 0.0712 wR_2 = 0.1742
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.744/–0.415	0.517/–0.399	0.898/–0.966	0.632/–0.496

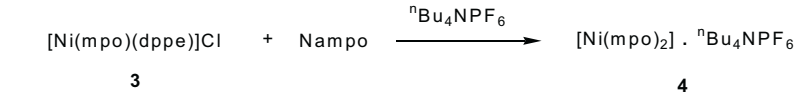
RESULTS AND DISCUSSION

Synthesis: In the preparation reactions of complexes **1**–**4**, the phosphorus containing ligands – trimethyl phosphite in the former and dppe in the latter (both will be called phosphine in the text for simplification) – reacted first with the metal salts to give the phosphine substituted chloride intermediates (in parentheses), which then were successively replaced by the mpo^- ligand bidentately, depending on the molar ratio of the reactants (an extra mole of Nampo added in **2** and **4**) or the reaction media ($^nBu_4NPF_6$ added), as depicted by the following reaction schemes:









Due to the univalent character of mpo^-, it is easy to balance the oxidation states of Co^{III} and Ni^{II} by chelation of mpo and fill up all coordination sites. This could also be the reason that multinuclear complexes with mpo ligands are rare, due to coordination saturation of the metal ions and thus difficult for further ligation. Auxiliary ions or ligands might be needed for polynuclear formation such as in $[Na_3Co_4(mpo)_8(\mu_3\text{-}O)_2(DMF)_4]Br{\cdot}2DMF$ [5]. The reactions also showed that thiolates easily replace phosphine ligands on the metal sites and the reactions are clean, while polymeric precipitates were formed if the reaction processes were reversed (with thiolate added first) and no pure products could be obtained.

Structures: The molecular structures of **1** and **3** are depicted in Figures 1 and 2, respectively, while those of **2** and **4** are similar to those reported and will not be shown. Selected atomic distances and bond angles are listed in Table 2. The cobalt atoms in both **1** and **2** are hexacoordinate in distorted octahedral geometry due to the restriction of the 5-membered chelate rings formed by mpo, where the environment of Co(III) in **1** is $P_2O_2S_2$ with O atoms and P atoms in *cis*-positions, respectively, and the

S atoms in *trans*-, while that in **2** is O_3S_3 in *facial*-conformation. The Ni atoms in **3** and **4** are both tetracoordinated in distorted square planar geometry, with environment P_2OS in **3**, and O_2S_2 in **4** with the O and S atoms *cis* to each other, respectively. That is to say that the two mpo ligands are *cis*-oriented in both **1** and **4**, in contrast to that ob-

served in $Co(mpo)_2(PBu^n_3)$ or $Co(mpo)_2(Py)$ [6], where they are in *trans*-conformation in the basal plane of the square-pyramid of Co(II). In both sets of complexes, further reaction of the phosphine-thiolato complexes with mpo^- causes only replacement reactions, while the coordination geometry of the transition metal ions was not changed: each mpo ligand replaces two *cis*-positioned phosphorus ligations, no matter whether the P atoms are derived from phosphite or the bidentate dppe.

Table 2. Selected atomic distances (Å) and bond angles (°) for complexes **1**–**4**.

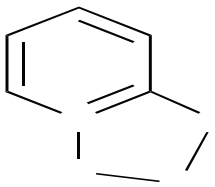
Complex **1**			
Co(1)–S(1)	2.205(4)	O(1)–Co(1)–S(1)	87.7(3)
Co(1)–S(2)	2.206(4)	O(2)–Co(1)–S(2)	86.6(3)
Co(1)–O(1)	1.930(9)	S(1)–Co(1)–S(2)	173.56(16)
Co(1)–O(2)	1.941(9)	O(1)–Co(1)–O(2)	87.1(4)
Co(1)–P(1)	2.127(5)	P(1)–Co(1)–P(2)	93.43(18)
Co(1)–P(2)	2.126(4)	P(1)–Co(1)–O(2)	175.9(3)
O(1)–N(1)	1.335(13)	P(2)–Co(1)–O(1)	176.0(3)
O(2)–N(2)	1.350(11)	O(1)–Co(1)–P(1)	89.0(3)
S(1)–C(1)	1.711(14)	O(1)–Co(1)–S(2)	88.0(3)
S(2)–C(6)	1.695(15)	O(2)–Co(1)–P(2)	90.4(3)
		O(2)–Co(1)–S(1)	88.4(3)
		Co(1)–S(1)–C(1)	97.2(5)
		Co(1)–S(2)–C(6)	96.5(5)
		Co(1)–O(1)–N(1)	115.8(8)
		Co(1)–O(2)–N(2)	117.4(8)
Complex **2**			
Co(1)–S(1)	2.196(2)	O(1)–Co(1)–S(1)	87.65(14)
Co(1)–S(2)	2.176(2)	O(2)–Co(1)–S(2)	88.30(14)
Co(1)–S(3)	2.194(2)	O(3)–Co(1)–S(3)	87.32(13)
Co(1)–O(1)	1.936(4)	S(1)–Co(1)–S(2)	91.14(8)
Co(1)–O(2)	1.939(4)	S(1)–Co(1)–S(3)	93.41(7)
Co(1)–O(3)	1.954(4)	S(2)–Co(1)–S(3)	91.23(8)
S(1)–C(5)	1.697(7)	O(1)–Co(1)–O(2)	88.13(18)
S(2)–C(10)	1.691(8)	O(1)–Co(1)–O(3)	89.43(19)
S(3)–C(15)	1.707(7)	O(2)–Co(1)–O(3)	88.11(18)
O(1)–N(1)	1.348(6)	O(1)–Co(1)–S(2)	176.20(14)
O(2)–N(2)	1.314(7)	O(2)–Co(1)–S(3)	175.38(15)
O(3)–N(3)	1.321(7)	O(3)–Co(1)–S(1)	177.02(16)
		Co(1)–O(1)–N(1)	116.1(3)
		Co(1)–O(2)–N(2)	115.8(3)
		Co(1)–O(3)–N(3)	115.1(3)
		Co(1)–S(1)–C(5)	97.5(2)
		Co(1)–S(2)–C(10)	96.4(3)
		Co(1)–S(3)–C(15)	97.2(2)
Complex **3**			
Ni(1)–O(1)	1.831(8)	O(1)–Ni(1)–S(1)	89.1(3)
Ni(1)–S(1)	2.149(4)	P(1)–Ni(1)–P(2)	86.68(13)
Ni(1)–P(1)	2.145(4)	O(1)–Ni(1)–P(1)	174.5(3)
Ni(1)–P(2)	2.186(4)	S(1)–Ni(1)–P(2)	171.76(15)

Table 2 (continuation)

O(1)–N(1)	1.354(13)	Ni(1)–O(1)–N(1)	117.2(7)
S(1)–C(5)	1.714(13)	Ni(1)–S(1)–C(5)	96.5(5)
Complex **4**			
Ni(1)–O(1)	1.844(4)	O(1)–Ni(1)–S(1)	89.57(14)
Ni(1)–O(2)	1.847(4)	O(2)–Ni(1)–S(2)	89.63(13)
Ni(1)–S(1)	2.130(2)	O(1)–Ni(1)–S(2)	175.80(14)
Ni(1)–S(2)	2.117(2)	O(2)–Ni(1)–S(1)	176.05(14)
O(1)–N(1)	1.338(6)	Ni(1)–O(1)–N(1)	116.9(3)
O(2)–N(2)	1.342(6)	Ni(1)–O(2)–N(2)	116.8(3)
S(1)–C(5)	1.702(7)	Ni(1)–S(1)–C(5)	96.9(2)
S(2)–C(10)	1.699(7)	Ni(1)–S(2)–C(10)	96.8(2)

The 5-membered mpo chelate rings in all complexes showed intramolecular synergism of the atoms, as exhibited by the structural parameters listed in Table 3, which also shows the respective data for some of the reported complexes [3,4,6–8]. The bonds S–C, O–N, and angles M–S–C and M–O–N showed constancy for all the complexes; an indication of rigidity and integrity of the 1,2-bidentate chelate rings, independent of the metal element, the coordination number or geometry. The only exception with obvious variations was observed in the bite angles O–M–S. Most of the complexes showed bite angles in the range 86–90°. However, large deviations are observed for the complexes *mer*-$[Fe(mpo)_3]$ (81.1°) and $[VO(mpo)_2]$ (82.2°) [8], in which the former has a meridionally coordinated Fe(III) atom and the latter a strongly electronegative oxo-atom doubly ligated to V(IV). The 5-coordinated complexes $[Co(mpo)_2L]$ (L = PBu^n_3 or Py) [6] and $[Zn(mpo)_2]_2$ [7] all exhibited slightly smaller O–M–S bite angles in range 83.1 ~ 83.9°. The small bite angle in *fac*-$[Cr(mpo)_3]\cdot Me_2CO$ (83.3°) could be caused by weak edge-H····π and π····π interactions and CH····O hydrogen bondings between the $Cr(mpo)_3$ molecules and between them and the acetone solvates.

Table 3. Comparison of average structural parameters (Å or °) in the chelating ligand mpo:



Complex	S–C	O–N	O–M–S	M–S–C	M–O–N
1	1.703	1.343	87.15	96.85	116.6
2	1.698	1.328	87.76	97.03	115.7
$Co(mpo)_3$[a]	1.716	1.348	88.0	96.8	116.0
$Co(mpo)_3$[b]	1.73	1.36	91.6	96.2	116.3

complex **4**, two inversely positioned $Ni(mpo)_2$ molecules form two weak H-bonds between one of the oxo-atom of one molecule with the α-proton in the pyridyl ring of another molecule with O–C distance of 2.567 Å.

Spectroscopic studies: All four complexes exhibit typical mpo absorptions $\nu_{C\text{-}S}$, $\nu_{N\text{-}O}$, and ν_{Py}. The characteristic feature of the C–S absorptions in range 1140–1180 cm^{-1} is an indication of partial C=S double bond character for mpo^{1-} as compared to that of the free Hmpo ligand (single peak at 1142 cm^{-1}), which was first established by Jones and Katritzky [10] to be a sign of the presence of thione form. The N–O bond and pyridyl ring absorb in range 1068–1096 cm^{-1} and 617–630 cm^{-1}, respectively. The trimethyl phosphite ligand $P(OMe)_3$ in **1** is identified by a strong peak at 1032 cm^{-1} for the P–O absorption, similar to those reported previously [9]. The anion PF_6^- in **1**, **2**, and **4** is characterized by the two absorptions near 840(s) and 550(m) cm^{-1}. The M–P or M–S absorptions in all complexes are quite weak and not identifiable probably due to the symmetric arrangement of atoms in the molecules.

FAB-MS study on **1** not only showed the molecular ion peak for $[Co(mpo)_2\{P(OMe)_3\}_2]^+$, but also exhibited fragments for the decomposition process of the complex as follows:

$$[Co(mpo)_2\{P(OMe)_3\}_2]^+ \xrightarrow{-P(OMe)_3} [Co(mpo)_2\{P(OMe)_3\}]^+$$

559(34%) 435(13%)

$$\xrightarrow{-P(OMe)_3} [Co(mpo)_2]+ \xrightarrow{-mpo-} [Co(mpo)]^{2+}$$

311(96%) 185(16%)

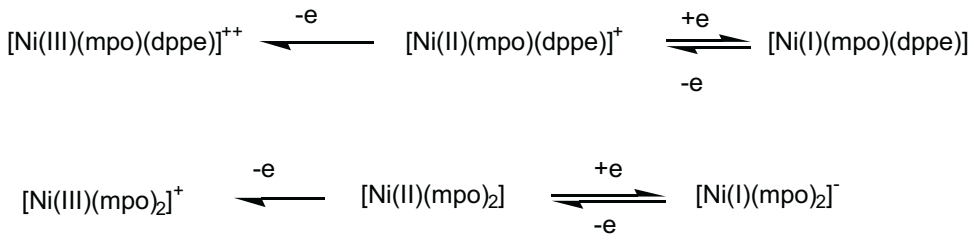
This fragmentation pattern can be considered as the retro-reaction of the synthetic process in which the phosphine ligands are better leaving groups than the mpo ligand, thus the $[Co(mpo)_2]^+$ ion is the most abundant and the most stable in the MS spectrum. From this scheme, the formation of **2** from **1** can be easily understood.

Electrochemical studies: Cyclic voltammetric studies showed quite similar patterns for the pair of Co complexes **1** and **2**, implying that they have nearly identical redox properties whether $P(OMe)_3$ is present or not, as shown below:

$$[Co(mpo_2)\{P(OMe)_3\}_2]^{2+} \xleftarrow[-0.22\ V]{-e} [Co(mpo_2)\{P(OMe)_3\}_2]^+ \xrightarrow[-0.72\ V]{+e} [Co(mpo_2)\{P(OMe)_3\}_2]^0$$

$$[Co(mpo)_3]^+ \xleftarrow[-0.25\ V]{-e} [Co(mpo)_3] \xrightarrow[-0.8\ V]{+e} [Co(mpo)_3]^-$$

This result indicates that the reduction and oxidation processes were caused by electron transfer at the central Co(III) site. The oxidation of the mpo ligand accounts for a second irreversible oxidation wave near to 1.10–1.15 V. For the pair of complexes **3** and **4**, the two CV curves are also quite similar with one redox couple ($E_{1/2}$ for **3**: –1.29 V; $E_{1/2}$ for **4**: –1.30 V) for Ni(II)/Ni(I), and one oxidation wave near 0.85–0.90 V for the irreversible oxidation of Ni(II) to Ni(III), accompanied by chemical decomposition of the Ni(III) species. The redox processes could be interpreted as follows:



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