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X-ray Structure of Dimeric $[Co(poph)(NCS)_2]_2$, an *N*-Oxide-bridged Cobalt(II) Complex with 2-Pyridinecarboxaldehyde 1-Oxide 2′-Pyridinylhydrazone (poph)

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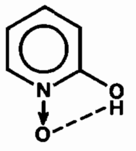
Abstract

An X-ray structure determination is reported for the *N*-oxide-bridged dimeric complex $[Co(poph)(NCS)_2]_2$ with 2-pyridinecarboxaldehyde 1-oxide 2′-pyridinylhydrazone (poph). The complex is monoclinic, $P2_1/c$, with $a = 12.460(7)$, $b = 9.884(3)$, $c = 16.562(8)$ Å, $\beta = 127.60(2)°$ and $Z = 4$. The ligand coordinates as a planar ONN tridentate via the *N*-oxide oxygen and the hydrazone and pyridyl nitrogens. A second out-of-ligand-plane bond from the *N*-oxide oxygen to another cobalt produces a centrosymmetric *N*-oxide-bridged structure. The in-ligand and out-of-ligand-plane Co–O distances are 2.028(5) and 2.460(5) Å, respectively. Each cobalt(II) is octahedrally coordinated by two *cis*-N-bonded thiocyanates, by an ONN-bonded poph molecule, and by a bridging *N*-oxide oxygen. This is the first structure report of a pyridine *N*-oxide-bridged cobalt(II) complex.

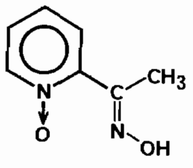
Introduction

Metal complexes of pyridine *N*-oxide and its substituted derivatives have been extensively investigated [1]. Many *N*-oxide-bridged copper(II) complexes, displaying strong magnetic interaction, have been obtained [1, 2], but few pyridine *N*-oxide-bridged complexes have been reported with other transition metal ions [3, 4].

In this laboratory we have been investigating ligands based on pyridine *N*-oxide, with donor substituents in the 2- and 2,6-positions, to see whether *N*-oxide bridging may be obtained with a wider range of transition metal ions. We have studied ligands **I–IX** [5–12]. Some nickel(II) and cobalt(II) complexes with ligands **II**, **V**, **VI** and **VII** are antiferromagnetic and were therefore assigned *N*-oxide-bridged structures, but no direct evidence for *N*-oxide bridging was available to us [7, 9, 10].



I



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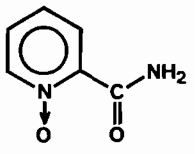

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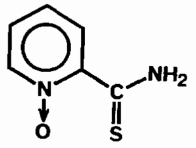

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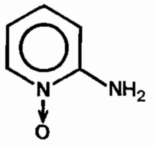

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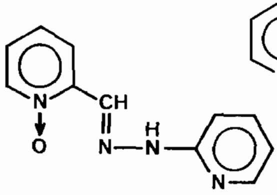
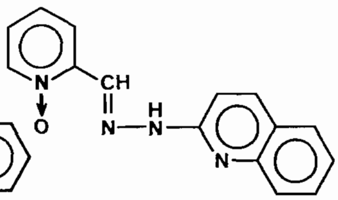
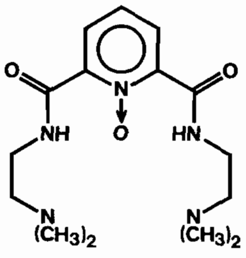


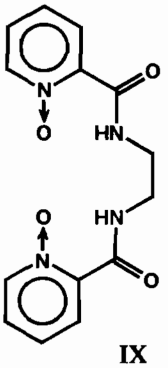
VI, poph



VII, poqh



VIII



IX

In particular, Landers and Phillips found that, with the ligand poph (**VI**) the complexes of cobalt(II) and nickel(II) halides and thiocyanates are antiferromagnetic and appear to be *N*-oxide-bridged [10]. With the ligand poqh (**VII**) the nickel(II) thiocyanate complex is apparently *N*-oxide-bridged, the nickel(II) halide complexes were assigned halide-bridged structures, and the cobalt(II) halide complexes are five-coordinate. There was no evidence

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for *N*-oxide bridging in the complexes of poph and poqh with copper(II) salts and with metal nitrates, because these complexes display no significant magnetic interaction [10].

In this paper, we report the X-ray crystal structure of the dimeric complex $[Co(poph)(NCS)_2]_2$ with 2-pyridinecarboxaldehyde 1-oxide 2′-pyridinylhydrazone (poph, **VI**). This is the first structure report of a pyridine *N*-oxide-bridged cobalt(II) complex. Many crystal structures involving pyridine *N*-oxide bridging are known with copper(II) complexes [1, 2] but the only one reported for another transition metal appears to be of $[Mn(dpco_2o)(H_2O)_2]_n$ (H_2dpco_2o = 2,6-pyridinedicarboxylic acid 1-oxide) [4].

Experimental

[Co(poph)(NCS)₂]₂

Single crystals of $[Co(poph)(NCS)_2]_2$ were obtained by the slow evaporation of a solution of poph (0.2 g) [10] and cobalt(II) thiocyanate (0.15 g) in absolute ethanol (100 ml).

Analyses and physical measurements

These were as previously described [6].

Crystallography

Crystal data

$C_{13}H_{10}CoN_6OS_2$, *M*, 389.32; monoclinic, space group $P2_1/c$; *a*, 12.460(7); *b*, 9.884(3); *c*, 16.562(8) Å; *β*, 127.60(2)°; *V*, 1616(1) Å^3; D_c, 1.60 g cm^{-3}, *Z*, 4; μ_{Mo}, 13.18 cm^{-1}. Crystal size: 0.03 × 0.15 × 0.15 mm, max. and min. transmission coefficients 0.78 and 0.92.

Structure determination

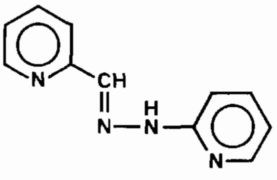
Intensities for 2835 reflexions were measured for a plate of somewhat uneven thickness with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode, using graphite monochromatized molybdenum radiation (λ 0.7107 Å) and $2\theta_{max}$ of 50°. Data were corrected for absorption. A total of 1547 reflexions with $I > 3\sigma(I)$ were considered observed, and were used for least-squares refinement after structure solution by direct phasing and Fourier methods. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located in difference Fouriers and given isotropic temperature parameters equivalent to those of the atoms to which bonded.

The final residuals *R*, R_w were 0.050, 0.060. Reflexion weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [13]. Structure solution was by MULTAN 80 [14], and refinement used BLOCKLS, a local version of ORFLS [15]. Cyber 172 and IBM3090 computers were used for all calculations.

Results and Discussion

A perspective diagram [16] of the structure is shown in Fig. 1. Atomic parameters, bond lengths and bond angles are given in Tables 1, 2 and 3, respectively. The complex is a centrosymmetric *N*-oxide-bridged dimer. Each cobalt(II) is octahedrally coordinated by two *cis*-N-bonded thiocyanates, by an ONN-bonded poph molecule, and by a bridging *N*-oxide oxygen. The octahedral coordination to the cobalt is rather distorted, the X–Co–Y angles being in the ranges 72.0–105.8(3)° and 147.2–171.3(2)°. The Co–N distances for the coordinated thiocyanates are 1.984(7) and 2.045(7) Å, similar to corresponding values of 2.036–2.116 Å found for other cobalt(II) systems [17–21].

No previous structures of complexes with poph have been reported. The structure is known [22], however, of the five-coordinate complex *β*-$[Co(paphy)Cl_2]$, in which paphy is 2-pyridinecarboxaldehyde 2′-pyridinylhydrazone (**X**).



X, paphy

The ligand paphy is the NNN-donor of which poph is the *N*-oxide derivative. In $[Co(poph)(NCS)_2]_2$ the Co–N(4) and Co–N(2) distances, involving the pyridine and hydrazone nitrogens, are 2.086(6) and 2.142(6) Å, respectively; the corresponding distances in *β*-$[Co(paphy)Cl_2]$ are 2.114(14) and 2.082(9) Å. The N(2)–Co–N(4) chelate angle of 76.1(2)° in $[Co(poph)(NCS)_2]_2$ is close to the corresponding angle of 75.0(5)° in *β*-$[Co(paphy)Cl_2]$.

The dimeric structure of $[Co(poph)(NCS)_2]_2$ involves a base to base combination of tetragonal pyramidal $Co(poph)(NCS)_2$ entities. In each of these entities the poph ligand and one coordinated thiocyanate produce the basal planar coordination. The bridging Co–O bond is 'out-of-ligand-plane', i.e. at right angles to the plane of the poph molecule. The Co–O distances are 2.028(5) Å for the 'in-ligand-plane' bond and 2.460(5) Å for the 'out-of-ligand-plane' bridging bond. The 'in-ligand-plane'

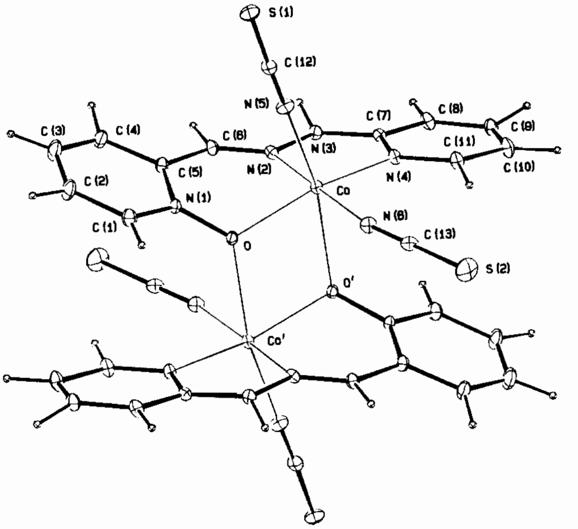


Fig. 1. A perspective drawing of $[Co(poph)(NCS)_2]_2$ with atom labelling.

TABLE 1. Non-hydrogen atomic parameters[a]

	x	y	z	B_{eq}
Co	0.4225(1)	0.6669(1)	0.4681(1)	2.32(4)
S(1)	0.0887(2)	0.8877(3)	0.4809(2)	4.01(11)
S(2)	0.7859(3)	0.8974(3)	0.7589(2)	6.84(16)
O	0.4012(5)	0.4806(5)	0.5081(3)	2.41(23)
N(1)	0.2765(6)	0.4314(6)	0.4643(4)	2.52(31)
N(2)	0.2868(6)	0.5803(6)	0.3191(4)	2.35(31)
N(3)	0.2964(6)	0.6385(6)	0.2489(4)	2.77(29)
N(4)	0.4564(6)	0.7804(6)	0.3794(4)	2.42(29)
N(5)	0.2621(7)	0.7569(8)	0.4513(5)	3.50(35)
N(6)	0.5680(7)	0.7492(7)	0.6014(5)	3.15(33)
C(1)	0.2496(9)	0.3815(9)	0.5262(6)	3.88(47)
C(2)	0.1270(10)	0.3247(11)	0.4889(7)	4.91(50)
C(3)	0.0314(10)	0.3163(11)	0.3853(8)	5.63(4)
C(4)	0.0579(9)	0.3653(9)	0.3220(6)	4.19(11)
C(5)	0.1799(8)	0.4270(8)	0.3614(6)	2.93(16)
C(6)	0.2004(8)	0.4883(9)	0.2907(6)	2.85(23)
C(7)	0.3857(8)	0.7423(8)	0.2809(5)	2.32(31)
C(8)	0.4107(9)	0.7990(8)	0.2161(5)	3.25(31)
C(9)	0.5050(10)	0.8988(9)	0.2539(6)	3.52(29)
C(10)	0.5757(10)	0.9420(9)	0.3542(6)	4.07(29)
C(11)	0.5455(9)	0.8801(9)	0.4130(6)	3.62(35)
C(12)	0.1862(9)	0.8096(9)	0.4611(5)	3.21(33)
C(13)	0.6588(9)	0.8116(9)	0.6675(6)	3.15(47)

[a]e.s.d.s in parentheses. B_{eq} (Å^2) is the isotropic equivalent of the anisotropic temperature factor.

Co–O bond length is similar to the cobalt *N*-oxide Co–O distance of 2.061(1) Å in the complex $[Co(pco_2o)_2(H_2O)_2]$ of 2-pyridinecarboxylic acid 1-oxide ($Hpco_2o$) [23].

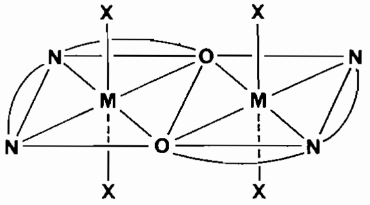
TABLE 2. Bond lengths (Å)[a]

Atoms	Distance
Co–O	2.028(5)
Co–N(2)	2.142(6)
Co–N(4)	2.086(6)
Co–N(6)	1.984(7)
Co–N(5)	2.045(7)
Co–O'	2.460(5)
C(1)–C(2)	1.370(11)
C(2)–C(3)	1.370(12)
C(3)–C(4)	1.365(11)
C(4)–C(5)	1.377(11)
C(5)–N(1)	1.361(9)
N(1)–C(1)	1.351(9)
N(1)–O	1.342(7)
C(5)–C(6)	1.472(10)
C(6)–N(2)	1.260(9)
N(2)–N(3)	1.367(7)
N(3)–C(7)	1.361(9)
C(7)–C(8)	1.403(9)
C(8)–C(9)	1.359(11)
C(9)–C(10)	1.391(11)
C(10)–C(11)	1.381(11)
C(11)–N(4)	1.326(10)
N(4)–C(7)	1.352(8)
N(5)–C(12)	1.174(10)
C(12)–S(1)	1.633(9)
N(6)–C(13)	1.161(9)
C(13)–S(2)	1.610(9)

[a]e.s.d.s in parentheses. ' indicates the symmetry transformation $1-x$, $1-y$, $1-z$.

The pyridine *N*-oxide and pyridine groups are not co-planar in poph. Rotation occurs about the C(5)–C(6) bond, tilting the pyridine *N*-oxide group relative to the pyridinehydrazone segment so that the *N*-oxide oxygen moves towards the cobalt in the adjacent $Co(poph)(NCS)_2$ entity. The extent of rotation is illustrated by the N(1)–C(5)–C(6)–N(2) torsional angle which is 21.7(13)°. No other significant distortion is present in the poph molecule.

An alternative to the 'out-of-ligand-plane' bridging in the structure would be the 'in-ligand-plane' bridging illustrated in **XI**. One reason for 'out-of-ligand-plane' bridging may be that there is less steric interaction between the poph molecules than would



XI

TABLE 3. Interatomic angles (°)[a]

Atoms	Angle
O–Co–N(2)	81.1(2)
O–Co–N(4)	147.2(2)
O–Co–N(5)	97.3(2)
O–Co–N(6)	102.8(2)
N(2)–Co–N(4)	76.1(2)
N(2)–Co–N(5)	89.9(2)
N(2)–Co–N(6)	171.3(2)
N(4)–Co–N(5)	105.8(3)
N(4)–Co–N(6)	97.0(2)
N(5)–Co–N(6)	97.3(3)
O–Co–O′	72.0(2)
O′–Co–N(2)	87.0(2)
O′–Co–N(4)	83.5(2)
O′–Co–N(5)	169.2(2)
O′–Co–N(6)	86.8(2)
Co–O–Co′	108.0(2)
O–N(1)–C(1)	117.7(6)
O–N(1)–C(5)	122.4(6)
C(1)–N(1)–C(5)	119.9(7)
N(3)–N(2)–C(6)	119.0(6)
N(2)–N(3)–C(7)	117.5(6)
C(7)–N(4)–C(11)	118.4(6)
N(1)–C(1)–C(2)	122.2(8)
C(1)–C(2)–C(3)	117.8(8)
C(2)–C(3)–C(4)	120.5(8)
C(3)–C(4)–C(5)	120.5(8)
N(1)–C(5)–C(4)	119.0(7)
N(1)–C(5)–C(6)	122.2(7)
C(4)–C(5)–C(6)	118.8(7)
N(2)–C(6)–C(5)	121.5(7)
N(3)–C(7)–N(4)	117.1(6)
N(3)–C(7)–C(8)	120.9(6)
N(4)–C(7)–C(8)	121.8(7)
C(7)–C(8)–C(9)	118.1(7)
C(8)–C(9)–C(10)	120.8(7)
C(9)–C(10)–C(11)	117.3(8)
N(4)–C(11)–C(10)	123.5(7)
S(1)–C(12)–N(5)	176.5(7)
S(2)–C(13)–N(6)	179.3(8)
N(1)–O–Co	119.4(4)
N(1)–O–Co′	119.9(4)
C(6)–N(2)–Co	127.8(5)
N(3)–N(2)–Co	113.2(5)
C(7)–N(4)–Co	116.0(5)
C(11)–N(4)–Co	125.6(5)
C(12)–N(5)–Co	167.5(6)
C(13)–N(6)–Co	166.0(6)

[a] e.s.d.s in parentheses. ′ indicates the symmetry transformation $1 - x$, $1 - y$, $1 - z$.

occur for 'in-ligand-plane' bridging. 'Out-of-ligand-plane' bridged structures are possible for the other *N*-oxide-bridged complexes of poph and poqh mentioned earlier, but the alternative 'in-ligand-plane' bridging arrangement cannot be ruled out. The infrared spectrum of $[Co(poph)(NCS)_2]_2$ contains two thiocyanate ν(CN) bands, at 2094 and 2068 cm^{-1}. This is in keeping with the 'out-of-ligand-plane' bridged structure, with the anions in non-equivalent environments. However, single ν(CN) bands were found [10] for $Ni(poph)(NCS)_2$ and $Ni(poqh)(NCS)_2 \cdot 0.5H_2O$; this is consistent with 'in-ligand-plane' bridged structures with the anions in equivalent environments.

The X-ray powder diffraction spectrum of the sample of $[Co(poph)(NCS)_2]_2$, prepared by Landers and Phillips, agrees with the spectrum calculated from the structure in this paper, showing that all of the sample of Landers and Phillips has the $[Co(poph)(NCS)_2]_2$ structure [24]. Landers and Phillips [10] found that $[Co(poph)(NCS)_2]_2$ has a μ_{eff} value of 4.32 BM at 298 K, decreasing to 3.86 BM at 89 K. The decrease in μ_{eff} of 0.46 BM from 298 to 89 K, and the associated Weiss θ value of -37 K, contrast with results for a range of complexes of the type $[Co(pxo)_2X_2]$ and $[Co(pco)_2X_2]$, with the *N*-oxide ligands **II** and **III**, to which monomeric structures were assigned [7, 8]. These complexes have μ_{eff} values of 4.99–4.44 BM at 298 K decreasing by 0.09–0.23 BM when cooled to 89 K, and θ values of -2 to -14 K. Landers and Phillips interpreted the greater decrease in μ_{eff} and the more negative θ value of $[Co(poph)(NCS)_2]_2$, compared to values for monomeric complexes, as indicating antiferromagnetism associated with *N*-oxide bridging [10]. The structure of $[Co(poph)(NCS)_2]_2$ is the first confirmation of this criterion for *N*-oxide bridging in cobalt(II) complexes, which was applied to several systems [7, 9, 10].

This paper supports the conclusion that poph produces *N*-oxide-bridged complexes. Varying degrees of magnetic interaction were found with the poph and poqh complexes [10]. We are, therefore, determining X-ray structures of bridged poph and poqh complexes in order to see whether magnetic interaction may be correlated with bridging geometry in these complexes.

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