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X-ray structure of [dibromo(pco-*O*,*O*′)(pco-*O*)copper(II)] (pco = 2-pyridinecarboxamide 1-oxide), a simple structure which contains a unidentate and bidentate form of the same ligand

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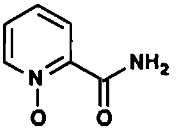
Abstract

The X-ray structure is reported for the complex $Cu(pco)_2Br_2$ of 2-pyridinecarboxamide 1-oxide (pco). The complex is triclinic, $P\bar{1}$, with $a = 7.431(7)$, $b = 7.869(10)$, $c = 13.739(13)$ Å, $\alpha = 91.04(7)$, $\beta = 90.83(7)$, $\gamma = 93.56(6)°$ and $Z = 2$. The complex is five-coordinate. Both bromide ions are coordinated. One pco molecule is bidentate, coordinating via the *N*-oxide and amide oxygen atoms. The other pco is unidentate, coordinating via the *N*-oxide oxygen, and with the amide group uncoordinated. In the unidentate pco molecule the uncoordinated amide group has its oxygen *trans* to the *N*-oxide oxygen, and there is strong hydrogen bonding between one of the amide hydrogens and the *N*-oxide oxygen. This hydrogen bonding may stabilise the unidentate behaviour of pco. Such hydrogen bonding is impossible with the analogous pyridine ligand 2-pyridinecarboxamide (pc) and this may explain why pc does not apparently act as a unidentate to simple metal salts. The IR spectrum of $Cu(pco)_2Br_2$ is compared with the spectra of other pco complexes which mostly appear to contain only bidentate pco.

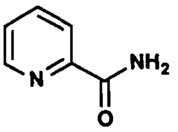
Introduction

Landers and Phillips [1] used 2-pyridinecarboxamide 1-oxide (pco, **I**) to obtain complexes of the type $M(pco)_2X_2$ ($M = Co^{II}, Ni^{II}, Cu^{II}$) together with $Mn(pco)Cl_2$ and $Cr(pco)_3Cl_3 \cdot 2H_2O$. The complexes were assigned six-coordinate structures. On the basis of IR spectra, the pco molecules were considered to be O,O-bidentates, coordinating through the *N*-oxide and amide oxygens.

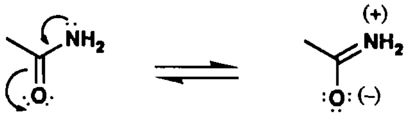
O-coordination by amide is expected to increase the contribution of canonical form (**IIIb**). This is expected to increase ν(CN) and decrease ν(CO) from the free ligand values. For O-bonded amide complexes, a rise in ν(CN) is usually found [2–5]. However, in some complexes such as those with 2-pyridinecarboxamide (pc, **II**), the expected decrease in ν(CO) does not occur but instead little change or even an increase is sometimes found [2, 4, 5]. This has been attributed to the effect of hydrogen bonding in the free ligand which lowers the ligand ν(CO) frequency [3, 5]. When complex formation occurs, O-coordination (which tends to decrease ν(CO)) and the concomitant breaking of hydrogen bonding (which tends to increase ν(CO)) may produce approximately cancelling effects. This could lead to no marked change in ν(CO) or even a moderate rise [3, 5].



I, pco



II, pc



IIIa **IIIb**

On complex formation with pco, in most cases, the ν(CN) frequency was found to rise (by *c.* 8–34 cm^{-1}) and ν(CO) to drop (by *c.* 3–22 cm^{-1}), from the free ligand values of 1374 cm^{-1} for ν(CN) and 1675 cm^{-1} for ν(CO) [1]. This indicates O-bonded amide with no serious complicating effects from hydrogen bonding [1]. The complex $Cu(pco)_2Br_2$ had, however, an unusual spectrum in that two ν(CO) bands were present. For $Cu(pco)_2Br_2$ one ν(CO) band occurred at 1666 cm^{-1}, i.e. lower than the free

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ligand ν(CO) and similar to the band in most other pco complexes, and the second band occurred at 1688 cm^{-1}, above the ligand value. In the complex $Cu(pco)_2(ClO_4)_2 \cdot CH_3OH$ two ν(CO) bands were likewise found, and in addition, two ν(CN) bands [1]. In view of these unusual spectra, we have carried out an X-ray structure analysis of $Cu(pco)_2Br_2$. The structure indicates the presence of both bidentate and unidentate pco.

Experimental

Cu(pco)$_2$Br$_2$

This was prepared by the method of Landers and Phillips [1] and single crystals were obtained by slow evaporation of an ethanolic solution of the complex.

Crystallography

Crystal data

$C_{12}H_{12}N_4O_4CuBr_2$, M 499.6, triclinic, space group $P\bar{1}$, $a = 7.431(7)$, $b = 7.869(10)$, $c = 13.739(13)$ Å, $\alpha = 91.04(7)$, $\beta = 90.83(7)$; $\gamma = 93.56(6)°$; $V = 802(1)$ Å^3, $Z = 2$; μ(Mo Kα) = 63.3 cm^{-1}, $D_c = 2.07$ g cm^{-3}, $D_o = 2.05$ g cm^{-3}. The irregularly shaped crystal had dimensions of *c.* 0.20×0.20×0.12 mm.

Structure determination

Intensities for 2820 reflections were collected on an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatised Mo Kα radiation ($\lambda = 0.71069$ Å). Data were corrected for absorption. A total of 2062 unique reflections with $I > 3\sigma(I)$ was considered observed. The structure was solved by Patterson heavy atom methods, and refined by a block diagonal least-squares procedure. All hydrogen atoms were found by difference maps and the final R factor was 0.040. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [6]. Structure solution and refinement computations were on a Cyber 172 computer and used local programs and BLOCKLS, a local version of ORFLS [7].

Results and discussion

The structure is illustrated in Fig. 1. Atomic parameters are listed in Table 1, and selected bond distances and bond angles are given in Table 2.

One pco molecule is bidentate and coordinates via the *N*-oxide and amide oxygens. The second pco is unidentate, coordinating via its *N*-oxide oxygen, but with an uncoordinated amide group. Two terminal bromides complete five-coordination on the copper(II). The coordination geometry can be described as either distorted trigonal bipyramidal or distorted square pyramidal. For the trigonal bipyramid, Br(1), Br(2) and O(2A) form the trigonal plane. The *N*-oxide oxygens, O(1A) and O(1B) take the axial positions, and are at angles of 6.4 and 5.3°, respectively, away from the normal to the plane. The angle O(1A)–Cu–O(1B) between the two axial bonds is 169.1(2)° and the copper atom is displaced by 0.016 Å out of the trigonal plane towards O(1A). The angles in the trigonal plane are 112.8(1), 116.9(2) and 130.3(2)°, not greatly different from the ideal angle of 120°. The square pyramidal description has Br(1), O(1A), O(2A) and O(1B) in the basal plane and Br(2) at the apex. The least-squares plane with Br(1), O(1A), O(2A) and O(1B) shows deviations of *c* ± 0.50 Å. The copper atom is 0.51 Å away from the basal plane towards Br(2) and the Cu–Br(2) vector is 4.0° from the normal to the least-squares plane. The geometry therefore seems to be closer to trigonal bipyramidal. The Cu–O and Cu–Br distances are all normal [8, 9]. There are small differences between Cu–X distances involving the *N*-oxide oxygens, and involving the Br atoms. These may be associated with factors such as unidentate and bidentate pco, apical and basal bonding in the square pyramidal description of the complex, and the hydrogen bonding described later.

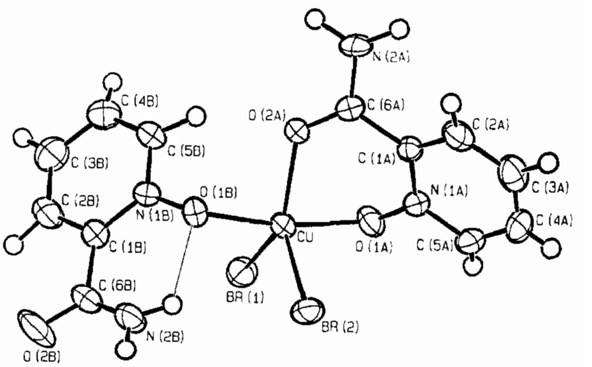

Fig. 1. A perspective drawing of the complex $Cu(pco)_2Br_2$.

In the bidentate ligand, the amide group is not coplanar with the pyridine *N*-oxide plane. The carbonyl oxygen, O(2A), is 0.45 Å away from the pyridine *N*-oxide plane, towards the copper, which is 1.31 Å above this plane. This results from a twist in the C(1A)–C(6A) bond, with the torsional angle N(1A)–C(1A)–C(6A)–O(2A) being 33(1)°.

The unidentate ligand is close to completely planar, with deviations of *c.* ± 0.05 Å from the least-squares plane through C(1B)–C(6B), N(1B), N(2B), O(1B) and O(2B). The amide group is disposed so that its oxygen, O(2B), is *trans* to the *N*-oxide oxygen, O(1B). The torsional angle N(1B)–C(1B)–C(6B)–N(2B) is

TABLE 1. Atomic parameters[a]

	x/a	y/b	z/c		x/a	y/b	z/c
Cu	0.6737(1)	0.6981(1)	0.6588(1)	C(4B)	0.2222(13)	0.6817(14)	0.8797(7)
Br(1)	0.6980(1)	0.4622(1)	0.7702(1)	C(5B)	0.3349(12)	0.7476(13)	0.8103(7)
Br(2)	0.9674(1)	0.8635(1)	0.6358(1)	C(6B)	0.7546(12)	0.8779(12)	0.9572(6)
C(1A)	0.5898(10)	0.7476(9)	0.4306(5)	N(1A)	0.7092(8)	0.6305(8)	0.4589(5)
C(2A)	0.6142(12)	0.8220(12)	0.3421(6)	N(2A)	0.2920(9)	0.8371(10)	0.4546(6)
C(3A)	0.7506(13)	0.7795(13)	0.2814(7)	N(1B)	0.5057(8)	0.8054(9)	0.8334(5)
C(4A)	0.8618(13)	0.6592(15)	0.3102(7)	N(2B)	0.8619(10)	0.9469(13)	0.8920(6)
C(5A)	0.8404(12)	0.5867(13)	0.3996(7)	O(1A)	0.6956(8)	0.5519(7)	0.5452(4)
C(6A)	0.4406(10)	0.7829(9)	0.4974(6)	O(2A)	0.4549(7)	0.7800(8)	0.5866(4)
C(1B)	0.5680(11)	0.8051(11)	0.9272(6)	O(1B)	0.6107(7)	0.8632(7)	0.7620(4)
C(2B)	0.4565(13)	0.7379(14)	0.9973(7)	O(2B)	0.7937(10)	0.8780(12)	1.0442(5)
C(3B)	0.2838(14)	0.6751(16)	0.9755(8)				

[a]e.s.d.s are given in parentheses.

TABLE 2. Selected interatomic distances (Å) and angles (°)

Cu–Br(1)	2.441(1)	Cu–Br(2)	2.498(1)
Cu–O(1A)	1.937(5)	Cu–O(1B)	1.987(5)
Cu–O(2A)	2.036(5)		
N(1A)–O(1A)	1.349(8)	N(1B)–O(1B)	1.331(8)
C(6A)–N(2A)	1.340(9)	C(6B)–N(2B)	1.311(12)
C(6A)–O(2A)	1.230(9)	C(6B)–O(2B)	1.227(10)
N(2B)–O(1B)	2.611(9)	N(2B)–O(2B)′	2.944(9)
Br(1)–Cu–Br(2)	112.8(1)	Br(2)–Cu–O(2A)	116.9(2)
Br(1)–Cu–O(1A)	92.6(2)	Br(2)–Cu–O(1B)	89.9(2)
Br(1)–Cu–O(2A)	130.3(2)	O(1A)–Cu–O(2A)	84.5(2)
Br(1)–Cu–O(1B)	94.4(2)	O(1A)–Cu–O(1B)	169.1(2)
Br(2)–Cu–O(1A)	95.0(2)	O(2A)–Cu–O(1B)	84.7(2)

1(1)°, in keeping with the overall planarity. The copper is 1.63 Å away from the ligand plane. The ligand is orientated in such a way that the amide nitrogen is at the non-bonded distance of 3.919(6) Å from the copper.

In the unidentate ligand, one hydrogen on the amide nitrogen, N(2B), is strongly intramolecularly hydrogen-bonded to the *N*-oxide oxygen, O(1B). The distance N(2B)–O(1B) is 2.611(9) Å, the van der Waals N–O distance being 2.9 Å [10]. This hydrogen bonding presumably helps to stabilise the *trans*-orientation of the amide oxygen, relative to the *N*-oxide oxygen; in this orientation chelate O,O-coordination by the ligand is impossible. The second hydrogen on N(2B) is intermolecularly hydrogen-bonded to the carbonyl oxygen, O(2B)′, on another unidentate molecule related by a centre of inversion, producing a dimeric arrangement with an N(2B)–O(2B)′ bond distance of 2.944(9) Å. One hydrogen on the amide nitrogen N(2A), in the bidentate pco molecule, is directed towards Br(2)″ in an adjacent complex at $1+x,y,z$ and this appears to be a hydrogen bond. The Br(2)″–H(2)N(2A) distance is 2.53(11) Å and the N(2A)–Br(2)″ distance is 3.504(9) Å, the van der Waals N–Br distance being 3.45 Å [10].

Conclusions

The occurrence of two ν(CO) bands for $Cu(pco)_2Br_2$ [1] is readily explained by the presence of unidentate and bidentate pco in the structure. The band at 1666 cm^{-1} is similar to the single band in most other pco complexes, thought to contain bidentate pco [1], and it may consequently be assigned to the coordinated amide in the bidentate pco. The band at 1688 cm^{-1} is therefore assigned to the uncoordinated amide; it is of higher frequency than the free ligand value and this may be due to weaker hydrogen bonding in the complex than in the free ligand. On the basis of IR spectra, the complex $Cu(pco)_2(ClO_4)_2 \cdot CH_3OH$ may also, therefore, contain unidentate and bidentate pco [1]. The ease of formation of pco complexes containing uncoordinated amide contrasts with the behaviour of pc (**II**), the pyridine analogue, which always appears to be bidentate when coordinated to simple metal salts [2, 4, 5, 11–15]. This difference between pco and pc may be due to the intramolecular hydrogen bonding of an uncoordinated amide hydrogen to the *N*-oxide oxygen in the unidentate pco, discussed above. Such hydrogen bonding is, of course, impossible in pc.

Supplementary material

All atom and thermal parameters, and all interatomic angles and torsional angles, are available from the authors on request.

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