

X-ray crystal structure of *cis*-[Co(pxo)₂Br₂] (pxo = 2-acetylpyridine 1-oxide oxime). Bis-chelate *cis*-octahedral complexes M(pxo)₂Hal₂ (M = Co^{II}, Ni^{II}; Hal = Cl, Br)

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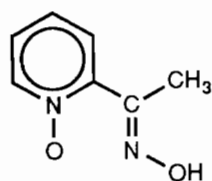
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Abstract

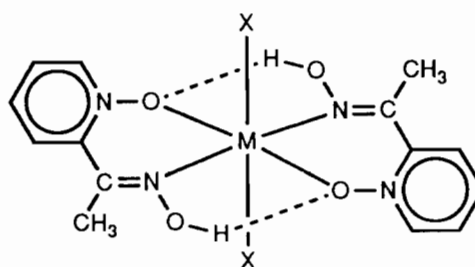
The X-ray structure is reported for the complex *cis*-[Co(pxo)₂Br₂] (pxo = 2-acetylpyridine 1-oxide oxime). The complex is monoclinic, *P*2₁/*c*, *a* = 12.167(3), *b* = 10.179(3), *c* = 16.863(4) Å β = 120.10(1)°. The complex has a bis-chelate *cis*-octahedral structure, involving ON bonded pxo, and the corresponding nickel(II) complex is isostructural. These results contrast with a previous assignment of *trans*-structures for these complexes. Hydrogen bonding from oxime to bromide appears to stabilise the *cis*-structure. On the basis of spectroscopic and magnetic measurements, the analogous chloride complexes, M(pxo)₂Cl₂ (M = Co^{II}, Ni^{II}), appear likewise to have *cis*-structures.

Introduction

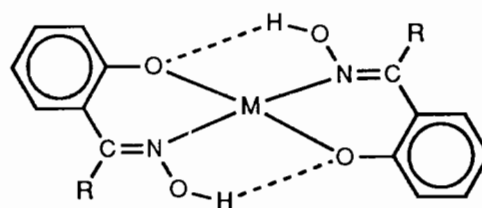
Landers and Phillips [1] reported bis-chelate cobalt(II) and nickel(II) complexes, M(pxo)₂X₂ (X = Br, NO₃, NCS), with 2-acetylpyridine 1-oxide oxime (pxo, I), a pyridine *N*-oxide oxime ligand. X-ray powder diffraction patterns showed that corresponding cobalt(II) and nickel(II) complexes were isostructural. The electronic spectra of the nickel(II) complexes indicated six-coordinate structures. With the nickel(II) bromide complex, Ni(pxo)₂Br₂, the ν₁(³T_{2g} ← ³A_{2g}) transition was split, indicating a considerable departure from O_h symmetry in this complex [2]. Because of this, Landers and Phillips proposed a *trans*-structure for Ni(pxo)₂Br₂, and for the isostructural complex Co(pxo)₂Br₂ (see II) [1].



I, pxo



II, *trans*-M(pxo)₂X₂ structures



III, structures of metal salicylaldoximates and derivatives

It was thought that these *trans*-structures in the M(pxo)₂Br₂ complexes might be stabilised by hydrogen bonding from oxime to *N*-oxide, as depicted in II. This proposed hydrogen bonding is analogous to that found in metal salicylaldoximate complexes and derivatives [3], which have an electronic similarity to bis-pxo complexes, as illustrated in III.

We have determined the X-ray crystal structure of [Co(pxo)₂Br₂] and find that, contrary to the assignment of Landers and Phillips [1], it has a *cis*-structure. Oxime

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to bromide hydrogen bonding is present, and this may help to stabilise the *cis*-configuration.

Experimental

Preparations

$[Co(pxo)_2Br_2]$ and $Ni(pxo)_2Br_2$

These were prepared by the method of Landers and Phillips [1]. Single crystals of $[Co(pxo)_2Br_2]$ were obtained by slow evaporation of an ethanolic solution of the complex.

$Co(pxo)_2Cl_2$

A hot solution of pxo [1] (1.60 g, 11.0 mmol) in 95% ethanol (50 ml) was added to a hot solution of cobalt(II) chloride hexahydrate (1.30 g, 5.5 mmol) in hot 95% ethanol (40 ml) and then left to cool; this gave a brick red solid which was dried in vacuum over $CaCl_2$ for two weeks. Yield 1.31 g (55%). *Anal.* Found: C, 38.89; H, 3.63; N, 12.66; Co, 13.78. Calc. for $CoCl_2C_{14}H_{16}N_4O_4$: C, 38.73; H, 3.71; N, 12.91; Co, 13.57%.

$Ni(pxo)_2Cl_2$

A hot solution of pxo (1.60 g, 11.0 mmol) in 95% ethanol (50 ml) was added to a hot solution of nickel(II) chloride hexahydrate (1.30 g, 5.5 mmol) in hot 95% ethanol (40 ml) and then left to cool; this gave a yellow-green solid which was dried in vacuum over $CaCl_2$ for two weeks. Yield 1.73 g (73%). *Anal.* Found: C, 38.78; H, 3.68; N, 12.81; Ni, 13.28. Calc. for $NiCl_2C_{14}H_{16}N_4O_4$: C, 38.75; H, 3.72; N, 12.91; Ni, 13.53%.

X-ray crystal structure determination of $[Co(pxo)_2Br_2]$

Intensities for 3547 reflections were collected for a crystal of dimensions $0.23 \times 0.23 \times 0.26$ mm with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatised Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Data were corrected for absorption. A total of 2490 unique reflections with $I > 3\sigma(I)$ was considered observed. Crystal data are given in Table 1. 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 0.028 (weighted value 0.034).

Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [4]. Structure solution and refinement computations used local programs and BLOCKLS, a local version of ORFLS [5].

TABLE 1. Crystal data for $[Co(pxo)_2Br_2]$

Molecular formula	$CoC_{14}H_{16}N_4O_4Br_2$
<i>a</i> (Å)	12.167(3)
<i>b</i> (Å)	10.179(3)
<i>c</i> (Å)	16.863(4)
β (°)	120.10(1)
<i>Z</i>	4
<i>D_c</i> (g/cm ³)	1.66
Space group	$P2_1/c$
μ_{Mo} (cm ⁻¹)	53.54
<i>V</i> (Å ³)	2088

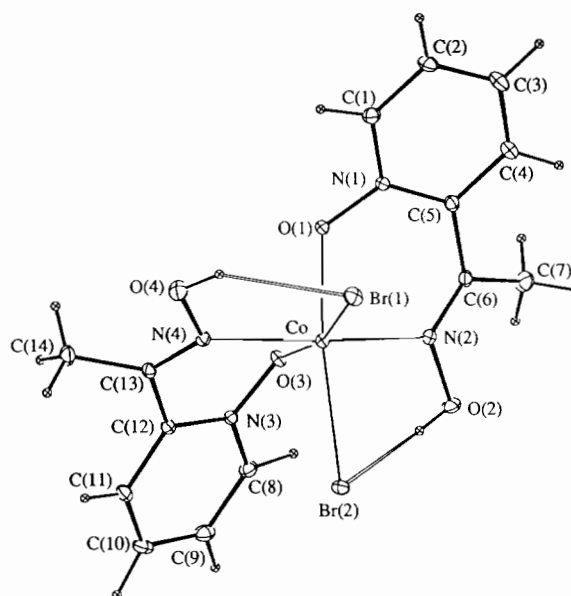


Fig. 1. A perspective drawing of the complex $[Co(pxo)_2Br_2]$.

Analyses and physical measurements

Microanalyses for carbon, hydrogen and nitrogen were carried out by Dr. H.P. Pham of the Microanalytical Laboratory, University of New South Wales. Metal analyses were carried out by Mr R.J. Finlayson, of the Department of Analytical Chemistry, using ICPAES techniques. IR spectra were obtained using a Perkin-Elmer 580B infrared spectrophotometer, and X-ray powder diffraction patterns were obtained using a Siemens D500 X-ray powder diffractometer with Cu $K\alpha$ radiation. Other physical measurements were as previously described [6].

Results and discussion

The structure is illustrated in Fig. 1. Atomic parameters are listed in Table 2, and selected bond distances and bond angles are given in Table 3.

TABLE 2. Atomic parameters^a

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Co	0.2347(0)	0.1833(0)	0.5479(0)
Br(1)	0.4717(0)	0.1628(0)	0.5951(0)
Br(2)	0.1739(0)	0.3575(0)	0.4206(0)
O(1)	0.2755(2)	0.0689(2)	0.6582(2)
O(2)	0.1534(3)	0.4394(3)	0.5934(2)
O(3)	0.0485(2)	0.1554(2)	0.5131(1)
O(4)	0.2850(3)	-0.0742(3)	0.4814(2)
N(1)	0.3630(3)	0.1047(3)	0.7421(2)
N(2)	0.2341(3)	0.3335(3)	0.6372(2)
N(3)	-0.0369(3)	0.1541(3)	0.4248(2)
N(4)	0.1892(3)	0.0170(3)	0.4611(2)
C(1)	0.4523(4)	0.0140(4)	0.7929(3)
C(2)	0.5405(4)	0.0379(4)	0.8825(3)
C(3)	0.5383(5)	0.1568(5)	0.9211(3)
C(4)	0.4491(4)	0.2466(4)	0.8683(3)
C(5)	0.3619(3)	0.2240(4)	0.7779(2)
C(6)	0.2678(4)	0.3255(3)	0.7220(2)
C(7)	0.2221(5)	0.4168(4)	0.7693(3)
C(8)	-0.1368(4)	0.2373(4)	0.3962(3)
C(9)	-0.2268(4)	0.2461(4)	0.3058(3)
C(10)	-0.2170(4)	0.1699(4)	0.2428(3)
C(11)	-0.1172(4)	0.0823(4)	0.2725(2)
C(12)	-0.0262(3)	0.0727(3)	0.3651(2)
C(13)	0.0806(3)	-0.0195(3)	0.3966(2)
C(14)	0.0574(4)	-0.1490(4)	0.3494(3)

^ae.s.d.s are given in parentheses.

TABLE 3. Selected interatomic distances (Å) and angles (°)^a

Co-N(2)	2.148(3)	Co-N(4)	2.116(3)
Co-O(1)	2.028(2)	Co-O(3)	2.047(2)
Co-Br(1)	2.575(0)	Co-Br(2)	2.582(0)
O(1)-Co-O(3)	84.0(1)	N(2)-Co-Br(1)	104.3(1)
O(1)-Co-N(2)	81.6(1)	N(2)-Co-Br(2)	89.5(1)
O(1)-Co-N(4)	91.6(1)	N(4)-Co-N(2)	163.7(1)
O(1)-Co-Br(1)	87.9(1)	N(4)-Co-Br(1)	90.1(1)
O(1)-Co-Br(2)	170.8(1)	N(4)-Co-Br(2)	96.5(1)
O(3)-Co-N(2)	84.1(1)	Br(1)-Co-Br(2)	96.3(0)
O(3)-Co-N(4)	80.4(1)	Br(1)-HO(4)-O(4)	148.5(2)
O(3)-Co-Br(1)	167.3(1)	Br(2)-HO(2)-O(2)	153.8(2)
O(3)-Co-Br(2)	93.2(1)		

^ae.s.d.s are given in parentheses.

The complex has an octahedral *cis*-structure, in contrast to the previously assigned *trans*-structure [1]. The pxo ligands chelate as ON donors, via the N-oxide and oxime groups, as proposed by Landers and Phillips [1]. The pyridine *N*-oxide and acetyloxime groups in the pxo molecules are both closely planar. The deviations of these groups from their least-squares planes are *c.* ±0.05 and ±0.009 Å, respectively in the C(1)–C(7) pxo molecule, and *c.* ±0.03 and ±0.008 Å, respectively, in the C(8)–C(14) pxo molecule. Twisting occurs, however, about the C(5)–C(6) bond in one pxo molecule

and about the C(12)–C(13) bond in the other pxo molecule. As a result, the dihedral angle between the pyridine *N*-oxide and oxime groups is 35.0° in the C(1)–C(7) pxo molecule and 36.1° in the C(8)–C(14) pxo molecule. The coordination to the cobalt(II) is close to octahedral, the X–Co–Y angles being in the ranges 80.4–104.3° and 163.7–170.8°. The Co–X bond lengths are normal.

Each bromide is hydrogen-bonded to an oxime hydrogen. The Br(1)–O(4) and Br(2)–O(2) distances are 3.190(3) and 3.162(3) Å, respectively. These are significantly shorter than the van der Waals Br–O distance of 3.3–3.5 Å [7], in keeping with the hydrogen bonding. This pxo---Br hydrogen bonding presumably helps to stabilise the meridional ONBr coordination, and hence the *cis*-structure, for the complex.

Measurements by Landers and Phillips [1] of X-ray powder diffraction patterns, which we have confirmed, show that [Co(pxo)₂Br₂] and Ni(pxo)₂Br₂ are isostructural. The Ni(pxo)₂Br₂ complex also, therefore, has a *cis*-structure.

With cobalt(II) and nickel(II) chlorides, Landers and Phillips obtained only the 1:1 complexes M(pxo)(CH₃OH)Cl₂ [1]. We have re-examined this system, and have isolated the 2:1 complexes M(pxo)₂Cl₂ (M = Co^{II}, Ni^{II}). The magnetic moment data for the 2:1 complexes (Table 4) are in keeping with monomeric structures. The diffuse reflectance spectrum for Ni(pxo)₂Cl₂ (Table 5 and Fig. 2) is typical of distorted octahedral nickel(II) [2] with bands $\nu_1(^3T_{2g} \leftarrow ^3A_{2g})$ and $\nu_2(^3T_{1g}(F) \leftarrow ^3A_{2g})$ occurring at *c.* 9000 and *c.* 15 000 cm⁻¹, respectively. The ν_1 band has a pronounced shoulder, indicating a lowering of symmetry, and it is resolved into two components at liquid nitrogen temperature. The spectrum of Ni(pxo)₂Cl₂ is very similar to that of Ni(pxo)₂Br₂ (Table 5 and Fig. 2) with bands shifted to higher frequency. This suggests that Ni(pxo)₂Cl₂ has a similar structure to Ni(pxo)₂Br₂. As mentioned above, Ni(pxo)₂Br₂ has a *cis*-structure because it is isostructural with [Co(pxo)₂Br₂], and so a similar structure is proposed for Ni(pxo)₂Cl₂.

The complex Co(pxo)₂Cl₂ has a diffuse reflectance spectrum in keeping with six-coordinate cobalt(II) [2] and very similar to that for [Co(pxo)₂Br₂] (Table 5).

TABLE 4. Magnetic data

Compound	μ_{eff} (BM)		θ (K) ^a
	304 K	89 K	
Ni(pxo) ₂ Cl ₂	3.15	3.16	0
Co(pxo) ₂ Cl ₂	4.88	4.79	-4

^aCorresponds to θ in $\chi'_M = C(T - \theta)^{-1}$.

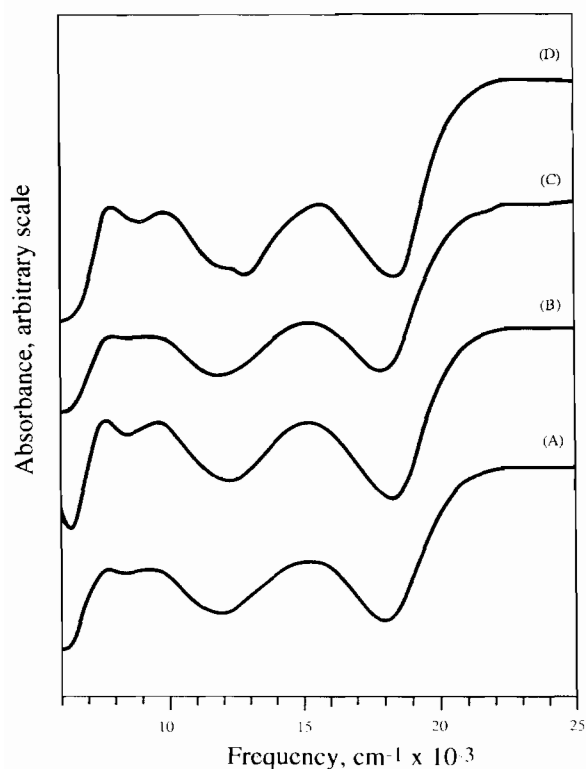


Fig. 2. Diffuse reflectance spectra. Ni(pxo)₂Br₂: at room temperature (A) and liquid nitrogen temperature (B); Ni(pxo)₂Cl₂: at room temperature (C) and liquid nitrogen temperature (D).

TABLE 5. Diffuse reflectance spectra

Compound	Temperature (K)	Absorption maxima ^a (cm ⁻¹ × 10 ⁻³)	Colour
Ni(pxo) ₂ Br ₂	298	7.7; 9.3; 15.2	yellow-green
	90	7.6; 9.7; 15.3	
Ni(pxo) ₂ Cl ₂	298	7.8, c. 9.5sh,b; 15.3	yellow
	90	7.8; 9.7; 15.6	
Co(pxo) ₂ Br ₂	298	7.6; 18.0	red
	90	7.7, c. 9.3sh; 18.1	
Co(pxo) ₂ Cl ₂	298	8.6b; 18.4	brick red
	90	7.8sh, 9.3; 18.4	

sh, shoulder; b, broad. ^aStrong ligand/charge transfer absorption commences at c. 20000 cm⁻¹ and extends through the higher frequency region in all spectra.

X-ray powder patterns show that Co(pxo)₂Cl₂ is isostructural with Ni(pxo)₂Cl₂ (Table 6) and we therefore propose a *cis*-structure for Co(pxo)₂Cl₂.

Most labile M(chelate)₂X₂ complexes (as with, for example, cobalt(II) or nickel(II)) have *trans*-structures. Where *cis*-structures occur, they have in some cases been attributed to steric factors, as with 2,2'-bipyridine complexes [8]. With ethylenediamine, both *cis*- and *trans*-Ni(en)₂XX' species are known [9] and hydrogen bonding appears to contribute to the stabilisation of

TABLE 6. Major lines in the X-ray powder diffraction patterns of Co(pxo)₂Cl₂ and Ni(pxo)₂Cl₂ (2θ° is for Cu Kα radiation)

Co(pxo) ₂ Cl ₂ (2θ°)	Ni(pxo) ₂ Cl ₂ (2θ°)
10.50vw	10.65vw
12.97vs	13.00s
14.86s	14.90s
15.40vw	15.46vw
19.50vw	19.54vw
21.20m	21.20m
22.40s	22.40s
24.35m	24.36m
26.04s	26.02s
27.40s	27.39s
28.35w	28.35w
29.32vw	29.39vw
31.15m	31.15m
32.00w	32.02w
33.50w	33.50w

vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

some of the *cis*-complexes [9b,d,e,g]. The 2:1 pxo metal halide complexes, described here, appear to form a new system in which hydrogen bonding is associated with the formation of *cis*-complexes.

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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References

- 1 A.E. Landers and D.J. Phillips, *Inorg. Chim. Acta*, 59 (1982) 41.
- 2 A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd edn., 1984.
- 3 (a) A. Chakravorty, *Coord. Chem. Rev.*, 13 (1974) 1; (b) M. Gallagher, M.F.C. Ladd, L.F. Larkworthy, D.C. Povey and K.A.R. Salib, *J. Crystallogr. Spectrosc. Res.*, 16 (1986) 967; (c) K. Zhou, C. Zhou, X. Chen and C. Yuan, *Kexue Tongbao (Foreign Lang. Ed.)*, 30 (1985) 1484; (d) L.F. Larkworthy and D.C. Povey, *J. Crystallogr. Spectrosc. Res.*, 13 (1983) 413.
- 4 J.A. Ibers and W.C. Hamilton (eds.), *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch, Birmingham, UK, 1974.
- 5 W.R. Busing, K.O. Martin and H.A. Levy, *ORFLS*, Oak Ridge National Laboratory, TN, 1962.

- 6 A.E. Landers and D.J. Phillips, *Inorg. Chim. Acta*, 51 (1981) 109.
- 7 J.E. Huheey, *Inorganic Chemistry – Principles of Structure and Reactivity*, Harper and Row, New York, 3rd edn., 1983.
- 8 J. Reedijk, in G. Wilkinson (ed.), *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford, 1987.
- 9 (a) L. Sacconi, F. Mani and A. Bencini, in G. Wilkinson (ed.), *Comprehensive Coordination Chemistry*, Vol. 5, Pergamon, Oxford, 1987; (b) E. Uhlig, *Coord. Chem. Rev.*, 10 (1973) 227; (c) L. Kh. Minacheva, A.S. Antsyshkina and M.A. Porai-Koshits, *Zh. Strukt. Khim.*, 15 (1974) 478; (d) A.A.G. Tomlinson, M. Bonamico, G. Dessy, V. Fares and L. Scaramuzza, *J. Chem. Soc., Dalton Trans.*, (1972) 1671; (e) M.E. Farago, J.M. James and V.C.G. Trew, *J. Chem. Soc. A*, (1967) 820; (f) M.A. Porai-Koshits, A.E. Shvelashvili, A.S. Antsyshkina and L.Kh. Minacheva, *Zh. Neorg. Khim.*, 13 (1968) 1245; (g) M.A. Poraj-Kosic, *Acta Crystallogr.*, 21 (1966) A 149.