Table 3. *Comparison of similar trans-*[Pt(dmso)(N-binding)Cl_2] *compounds*

Compound	Pt—S (Å)	Pt—N (Å)	Pt—Cl (Å)	Reference
trans-[Pt(dmso)(cytidine)Cl_2]	2.220 (4)	2.034 (13)	2.291 (5), 2.310 (4)	Melanson & Rochon (1978*a*)
trans-[Pt(dmso)(2-picoline)Cl_2]	2.212 (3)	2.046 (10)	2.282 (3), 2.295 (4)	Melanson & Rochon (1978*b*)
trans-[Pt(dmso)(NH_3)Cl_2]	2.209 (1)	2.053 (4)	2.296 (1), 2.306 (1)	Viossat, Khodadad & Rodier (1991)
trans-[Pt(dmso)(pyridine)Cl_2]	2.224 (2)	2.052 (6)	2.299 (3), 2.276 (3)	
	2.225 (3)	2.061 (10)	2.305 (2), 2.294 (3)	Caruso, Spagna & Zambonelli (1980)
trans-[Pt(dmso)(isopropylamine)Cl_2]	2.220 (2)	2.067 (6)	2.315 (2), 2.290 (2)	Melanson & Rochon (1984)
trans-[Pt(dmso)(piperidine)Cl_2]	2.212 (6)	2.083 (18)	2.292 (6), 2.296 (5)	This work

allow any firm conclusions to be drawn about the *trans* influence of S on the piperdine N atom compared to that on other types of N atom.

Experimental

Crystal data

[Pt(C_2H_6OS)($C_5H_{11}N$)Cl_2]
M_r = 429.26
Orthorhombic
$P2_12_12_1$
a = 9.551 (2) Å
b = 10.486 (3) Å
c = 12.543 (2) Å
V = 1256.2 (3) Å^3
Z = 4
D_x = 2.273 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 4.9–15.5°
μ = 11.86 mm^{-1}
T = 295–296 K
Prism
0.22 × 0.18 × 0.05 mm
Yellow-orange

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: by integration from crystal shape
T_{min} = 0.1986, T_{max} = 0.4152
1746 measured reflections
1746 independent reflections
1329 observed reflections [$I>3\sigma(I)$]

R_{int} = 0.0068 (based on standard reflections)
θ_{max} = 28°
h = 0 → 12
k = −13 → 0
l = 0 → 16
3 standard reflections frequency: 120 min intensity variation: < ±2%

Refinement

Refinement on F
Final R = 0.048
wR = 0.061
S = 1.04
1329 reflections
119 parameters
H-atom parameters not refined
$w = (\sigma^2/4|F_o|^2+0.038|F_o|^2+3.0)^{-1}$
$(\Delta/\sigma)_{max}$ = 0.076

$\Delta\rho_{max}$ = 1.46 e Å^{-3}
$\Delta\rho_{min}$ = −1.32 e Å^{-3}
Extinction correction: isotropic
Extinction coefficient: 370
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

The structure was solved by standard Patterson and difference Fourier methods and refined by full-matrix least-squares calculations employing programs amended by Lundgren (1982). The final coordinates are given in Table 1. The H atoms could not be located in difference Fourier maps and were not included in the structure-factor calculations.

Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

0108-2701/92/112075-04$06.00

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55293 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1016]

References

Bengtsson, L. A. & Oskarsson, Å. (1992). *Acta Chem. Scand.* **46**, 707–711.
Boström, D., Strandberg, R., Norén, B. & Oskarsson, Å. (1991). *Acta Cryst.* C**47**, 2101–2104.
Bugarcic, Z., Norén, B., Oskarsson, Å., Stålhandske, C. & Elding L. I. (1991). *Acta Chem. Scand.* **45**, 361–366.
Caruso, F., Spagna, R. & Zambonelli, L. (1980). *Acta Cryst.* B**36**, 713–715.
Kukushkin, Yu. N., Vyaz'menskii, Yu. E. & Zorina, L. I. (1968). *Russ. J. Inorg. Chem.* **13**(11), 1573–1576.
Lundgren, J. O. (1982). *Crystallographic Computer Programs.* Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.
Melanson, R. & Rochon, F. D. (1978*a*). *Inorg. Chem.* **17**(3), 679–681.
Melanson, R. & Rochon, F. D. (1978*b*). *Acta Cryst.* B**34**, 1125–1127.
Melanson, R. & Rochon, F. D. (1984). *Acta Cryst.* C**40**, 793–795.
Viossat, B., Khodadad, P. & Rodier, N. (1991). *Acta Cryst.* C**47**, 1316–1317.

Acta Cryst. (1992). C**48**, 2075–2078

Regioselective Pyrazine Ring Reduction of 4-(Quinoxalin-2-yl)-1,3-dithiole-2-thione

Roy L. Beddoes, James R. Russell, C. David Garner and John A. Joule*

Chemistry Department, University of Manchester, Manchester M13 9PL, England

(*Received* 27 *February* 1992; *accepted* 5 *June* 1992)

Abstract

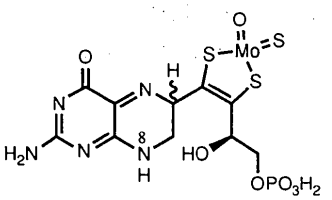
The crystal structure of 4-(4-benzyloxycarbonyl-1,2,3,4-tetrahydroquinoxalin-2-yl)-1,3-dithiole-2-thione [benzyl 1,2,3,4-tetrahydro-3-(2-thioxo-1,3-dithiol-4-yl)quinoxaline-1-carboxylate] shows that

© 1992 International Union of Crystallography

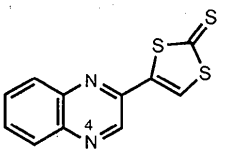
treatment of the precursor quinoxaline with a combination of sodium cyanoborohydride and benzyl chloroformate achieves both selective saturation and selective N4 protection of the pyrazine ring. The crystal was shown to include 17% co-crystallized 4-(7-bromo-4-benzyloxycarbonyl-1,2,3,4-tetrahydroquinoxalin-2-yl)-1,3-dithiole-2-thione. The dithiolene ring makes a dihedral angle of *ca* 90° to the average plane of the tetrahydropyrazine ring. Both urethane and secondary aromatic amine N atoms are essentially planar. The benzyloxycarbonyl and dithiole units lie on the same side of the tetrahydroquinoxaline unit.

Comment

We are developing a synthetic route (Rowe, Garner & Joule, 1985; Larsen, Garner & Joule, 1989; Larsen, Rowe, Garner & Joule, 1989) to Moco (1) (Johnson, 1980; Rajagopalan, 1991; Gardlik & Rajagopalan, 1990) which is the cofactor of all molybdoenzymes except nitrogenase. The route is being developed in part using quinoxalines instead of the less tractable pteridines. The ene–dithiolate unit, which complexes the molybdenum in Moco, is to be carried protected through later stages of the synthesis as a 1,3-dithiole-2-thione; it has been shown that such units can be used as either indirect (Boyde, Garner, Joule & Rowe, 1987) or direct (Armstrong, Austerberry, Beddoes, Helliwell, Joule & Garner, 1992) precursors of ene–dithiolate metal complexes. It is planned that the production of the requisite dihydropyrazine oxidation level, *cf.* (1), will involve reduction to tetrahydro level then regioselective reoxidation to dihydro level; this strategy will require regioselective N-8 protection. We sought to model this sequence using quinoxalinyldithiole (2), aiming for reduction of the pyrazine ring while leaving the dithiole untouched and regioselective N-4 protection.

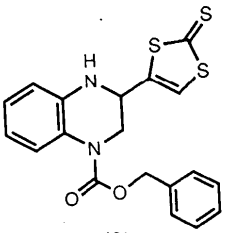


(1)



(2)

4-(Quinoxalin-2-yl)-1,3-dithiole-2-thione (Rowe, Garner & Joule, 1985) was reduced (Russell, Garner & Joule, 1992) at room temperature with sodium cyanoborohydride in $MeOH/CH_2Cl_2$ (1:1) in the presence of benzyl chloroformate to produce a tetrahydro derivative carrying one *N*-benzyloxycarbonyl substituent, the location of which could not be assigned unambiguously by spectroscopic analysis. X-ray analysis showed the product (3) to have the desired structure with the urethane at N-4.



(3)

The atomic parameters for the non-H atoms of (3) are listed in Table 1, Table 2 lists selected bond lengths and bond angles, and Fig. 1 shows a *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule with the crystallographic numbering system. The analysis shows the dithiole ring to be oriented at close to 90° to the average plane of the tetrahydroquinoxaline and each N atom to be planar, the sums of angles at each being 360.0°. Interestingly, both benzyloxycarbonyl and dithiole (the substituents on the tetrahydroquinoxaline) lie on the same side of the bicyclic ring.

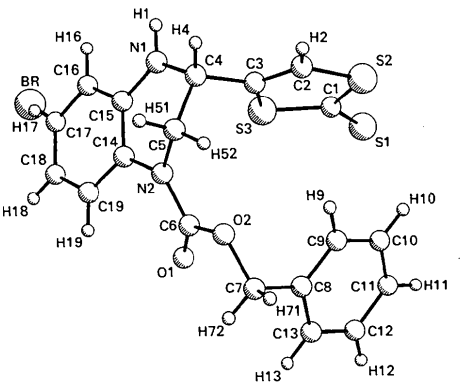


Fig. 1. *PLUTO* drawing of tetrahydroquinoxaline (3) showing the crystallographic numbering scheme.

The first step in the chemical synthesis of the quinoxalinedithiole (2) is the conversion of 2-acetylquinoxaline into 2-bromoacetylquinoxaline. During refinement, an additional electron-density peak appeared at about 1.8 Å from C17 (see Fig. 1 for numbering). This could not be attributed to water and was eventually recognized as bromine. Refinement then proceeded smoothly to an acceptable molecular geometry and produced a value of 17% bromine at the H17 site. A re-examination of the crystalline material, using microanalytical techniques, confirmed the presence of bromine in an amount corresponding to 14.9% brominated derivative in the sample.

We conclude that during the side-chain halogenation, which comprised the first synthetic step,

some additional benzene-ring bromination of the heterocycle occurs at the quinoxaline C-7 position and that, surprisingly, this ring-brominated material is carried through the three subsequent chemical steps, including three purifications by recrystallization, leading to the sample examined in this study. It seems remarkable not only that a not insubstantial impurity should have been carried through the sequence, but also that the result was a crystallographically acceptable solid in which a large Br atom occupies the site of a hydrogen in 17% of the sample.

Experimental

Crystal data

$0.83C_{19}H_{16}N_2O_2S_3.$-$0.17C_{19}H_{15}BrN_2O_2S_3$	$Z = 2$
$M_r = 400.53$ (major component)	$D_x = 1.473$ Mg m^{-3}
Triclinic	Cu $K\alpha$ radiation
$P\bar{1}$	$\lambda = 1.54178$ Å
$a = 12.073$ (2) Å	Cell parameters from 21 reflections
$b = 13.562$ (2) Å	$\theta = 39$-$40°$
$c = 6.2527$ (5) Å	$\mu = 4.15$ mm^{-1}
$\alpha = 101.05$ (9)°	$T = 296$ (1) K
$\beta = 103.38$ (8)°	Tabular
$\gamma = 70.76$ (1)°	0.450 × 0.200 × 0.020 mm
$V = 932.9$ (2) Å^3	Yellow

Data collection

Rigaku AFC-5*R* diffractometer	$R_{int} = 0.031$
$\omega/2\theta$ scans	$\theta_{max} = 60°$
Absorption correction: empirical	$h = -5 \rightarrow 13$
$T_{min} = 0.81$, $T_{max} = 1.16$	$k = -14 \rightarrow 15$
2917 measured reflections	$l = -7 \rightarrow 6$
2762 independent reflections	3 standard reflections monitored every 150 reflections
2177 observed reflections [$I>3.0\sigma(I)$]	intensity variation: −1.83%

Refinement

Refinement on F	$w = 4F_o^2/[\sigma^2(F_o^2)]$
Final $R = 0.054$	$(\Delta/\sigma)_{max} = 0.01$
$wR = 0.066$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
$S = 2.42$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
2177 reflections	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
245 parameters	
H-atom parameters derived stereochemically and not refined	

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = \tfrac{8}{3}\pi^2\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
S1	0.2845 (1)	0.0140 (1)	0.0388 (2)	5.44 (7)
S2	0.2697 (1)	0.1148 (1)	0.5019 (2)	5.19 (7)
S3	0.4603 (1)	0.1202 (1)	0.3098 (2)	4.70 (6)
O1	0.4448 (3)	0.3971 (3)	0.0869 (5)	5.1 (2)
O2	0.3437 (3)	0.4498 (2)	0.3686 (5)	4.6 (2)
Br	0.9987 (3)	0.0793 (3)	0.1661 (6)	5.8 (2)
N1	0.6676 (4)	0.1731 (3)	0.6320 (7)	5.0 (2)
N2	0.5340 (3)	0.3497 (2)	0.4306 (5)	3.7 (2)
C1	0.3347 (4)	0.0795 (3)	0.2711 (7)	4.4 (2)
C2	0.3687 (4)	0.1776 (3)	0.6669 (7)	4.6 (2)
C3	0.4568 (4)	0.1808 (3)	0.5790 (6)	3.8 (2)
C4	0.5537 (4)	0.2309 (3)	0.6971 (7)	4.3 (2)
C5	0.5216 (4)	0.3458 (3)	0.6567 (6)	4.1 (2)
C6	0.4408 (4)	0.3990 (3)	0.2781 (7)	3.7 (2)
C7	0.2407 (4)	0.5022 (4)	0.2163 (9)	5.4 (3)
C8	0.1791 (4)	0.4285 (3)	0.0673 (8)	4.4 (2)
C9	0.1609 (5)	0.3491 (4)	0.1502 (9)	5.6 (3)
C10	0.0976 (5)	0.2854 (4)	0.018 (1)	7.2 (4)
C11	0.0526 (5)	0.3001 (5)	−0.201 (1)	7.6 (4)
C12	0.0701 (5)	0.3785 (6)	−0.285 (1)	7.1 (4)
C13	0.1345 (5)	0.4425 (4)	−0.1528 (9)	5.7 (3)
C14	0.6484 (4)	0.2936 (3)	0.3775 (6)	3.6 (2)
C15	0.7140 (4)	0.2049 (3)	0.4848 (7)	4.0 (2)
C16	0.8263 (5)	0.1474 (4)	0.4368 (9)	5.3 (3)
C17	0.8727 (5)	0.1780 (4)	0.288 (1)	6.0 (3)
C18	0.8095 (5)	0.2678 (4)	0.1883 (8)	5.4 (3)
C19	0.6987 (4)	0.3255 (4)	0.2354 (7)	4.5 (2)

Table 2. *Geometric parameters* (Å, °)

S1—C1	1.650 (4)	N1—C15	1.378 (5)
S2—C1	1.714 (4)	N2—C5	1.468 (5)
S2—C2	1.726 (5)	N2—C6	1.369 (5)
S3—C1	1.730 (5)	N2—C14	1.422 (5)
S3—C3	1.729 (4)	C2—C3	1.322 (6)
O1—C6	1.203 (5)	C3—C4	1.519 (6)
O2—C6	1.340 (5)	C4—C5	1.533 (6)
O2—C7	1.445 (5)	C7—C8	1.495 (6)
Br—C17	1.868 (6)	C14—C15	1.399 (6)
N1—C4	1.449 (6)		
C1—S2—C2	97.5 (2)	C2—C3—C4	125.2 (4)
C1—S3—C3	97.6 (2)	N1—C4—C3	111.9 (3)
C6—O2—C7	114.5 (3)	N1—C4—C5	108.8 (3)
C4—N1—C15	123.4 (4)	C3—C4—C5	112.2 (4)
C5—N2—C6	122.7 (3)	N2—C5—C4	109.7 (3)
C5—N2—C14	115.0 (3)	O1—C6—O2	124.0 (4)
C6—N2—C14	122.2 (3)	O1—C6—N2	124.7 (4)
S1—C1—S2	124.3 (3)	O2—C6—N2	111.4 (3)
S1—C1—S3	123.6 (3)	O2—C7—C8	113.2 (4)
S2—C1—S3	112.1 (2)	N1—C15—C14	120.9 (4)
S2—C2—C3	117.0 (3)	N1—C15—C16	120.1 (4)
S3—C3—C2	115.8 (3)	N2—C14—C15	117.1 (4)
S3—C3—C4	119.0 (3)	N2—C14—C19	123.2 (4)

Computer programs used: *DIFABS* (Walker & Stuart, 1983); *SHELXS86* (Sheldrick, 1985); *TEXSAN* (Molecular structure Corporation, 1985); *PLUTO*. The structure was solved by direct methods using *SHELXS86*. Anomalous dispersion effects (Ibers & Hamilton, 1964) were included in F_c.

We thank SERC for a research fellowship (JRR) and for funds for the purchase of the Rigaku AFC-5*R* diffractometer.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry together with least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55213 (29 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1006]

References

Armstrong, A. M., Austerberry, M. S., Beddoes, R. L., Helliwell, M., Joule, J. A. & Garner, C. D. (1992). Unpublished.

Boyde, S., Garner, C. D., Joule, J. A. & Rowe, D. J. (1987). *J. Chem. Soc. Chem. Commun.* pp. 800–801.
Gardlik, S. & Rajagopalan, K. V. (1990). *J. Biol. Chem.* **265**, 13047–13054.
Ibers, J. A. & Hamilton, W. C. (1964). *Acta Cryst.* **17**, 781–782.
Johnson, J. L. (1980). In *Molybdenum and Molybdenum-Containing Enzymes*, edited by M. P. Coughlan, pp. 345–383. Oxford: Pergamon Press.
Larsen, L., Garner, C. D. & Joule, J. A. (1989). *J. Chem. Soc. Perkin Trans.* 1, pp. 2311–2316.
Larsen, L., Rowe, D. J., Garner, C. D. & Joule, J. A. (1989). *J. Chem. Soc. Perkin Trans.* 1, pp. 2317–2327.
Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.
Rajagopalan, K. V. (1991). In *Advances in Enzymology and Related Areas of Molecular Biology*, Vol. 64, edited by A. Meister, pp. 215–290. New York: John Wiley.
Rowe, D. J., Garner, C. D. & Joule, J. A. (1985). *J. Chem. Soc. Perkin Trans.* 1, pp. 1907–1910.
Russell, J. R., Garner, C. D. & Joule, J. A. (1992). *J. Chem. Soc. Perkin Trans.* 1, pp. 1245–1249.
Sheldrick, G. M. (1985). *SHELXS*86. In *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

Acta Cryst. (1992). C**48**, 2078–2080

Structure of a 'Hypervalent' Linear Bis(phthalimidato)bromate(I) Complex

MARGARETA ELDING,* ANN-KRISTIN LARSSON, GÖRAN SVENSSON AND JÖRGEN ALBERTSSON†

Inorganic Chemistry 2, *Chemical Center, University of Lund, PO Box* 124, *S*-22100 *Lund, Sweden*

LENNART EBERSON

MAX Chemistry, Chemical Center, University of Lund, PO Box 124, *S*-22100 *Lund, Sweden*

(*Received* 2 *March* 1992; *accepted* 8 *June* 1992)

Abstract

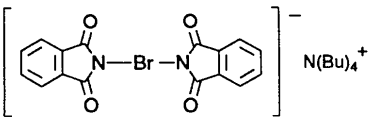
In tetrabutylammonium bis(phthalimidato)bromate(I) the anion is symmetric about Br, which is on a twofold axis. The Br atom is almost linearly coordinated by the two phthalimidato groups with N—Br—N = 176.0 (6)° and Br—N = 2.105 (8) Å. The dihedral angle between the least-squares plane of the two phthalimidato ligands is 87.0 (2)°. The electronic structure of Br can be described as an $sp^3d_{z^2}$ hybridization with three lone pairs in a plane perpendicular to the N—Br—N bond. The formal oxidation state of Br is +1.

† Present address: Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden.

0108-2701/92/112078-03$06.00 © 1992 International Union of Crystallography

Comment

The title compound (1) was investigated as part of a study of N—Br—N bonding properties. The complex was prepared as described by Barry, Finkelstein, Moore, Ross & Eberson (1984) and then recrystallized from an acetonitrile solution by the addition of diethyl ether and pentane. This yielded colourless needles which had the expected NMR spectra.



(1)

The bis(phthalimidato)bromate(I) ion (Fig. 1) is symmetric having equal Br—N distances as the Br atom is on a twofold axis (Table 1, Fig. 2). The coordination around Br is almost linear (Table 2), implying that the electrons around the Br atom are equally distributed between the two phthalimidato ligands. The Br—N distance is large compared to 1.817 (7) Å in *N*-bromosuccinimide (Jabay, Pritzkow & Jander, 1977), showing an increased electron density in the N—Br—N region of the title compound. There are ten electrons equally distributed around the Br atom, just as for Xe in XeF_2, I in IBr_2^- and the central Br in symmetric Br_3^-. In a simple electronic model the hybridization of Br can be described as $sp^3d_{z^2}$ with three lone pairs in the plane perpendicular to the N—Br—N bond. The electron-withdrawing phthalimidato ligands thus cause the formal oxidation state of Br to be +1. The least-squares planes of the two phthalimidato ligands are inclined at 87.0 (2)° with respect to each other. The O atoms are located within the planes, while the Br atom is 0.272 (2) Å out of both planes.

A short review of some structural parameters for compounds with linear N—Br—N bonding is given in Table 3. This shows that the average Br—N distance within a molecule is nearly constant, ranging from 2.102 to 2.142 Å. One short bond consequently results in the elongation of the other. This was also found for compounds with a linear N—I—N bond (Brock, Fu, Blair, Chen & Lowell, 1988). Table 3 also shows that the dihedral angle between the least-squares planes varies from 0 to 90°, indicating that the distance between the ligands is too long for them to interact. In *N,N'*-biphthalimide (Apreda, Foces-Foces, Cano & Garcia-Blanco, 1978) the distance between the two ring systems is shorter,