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## The Red–Violet Isomer of Dichlorobis[2-(*m*-tolyl)azopyridine]osmium(II)

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**Abstract.** [OsCl<sub>2</sub>(C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>)<sub>2</sub>],  $M_r = 655.6$ , triclinic,  $P\bar{1}$ ,  $a = 8.593$  (7),  $b = 10.78$  (1),  $c = 13.52$  (1) Å,  $\alpha = 79.10$  (8),  $\beta = 91.69$  (7),  $\gamma = 78.74$  (7)°,  $V = 1203$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $F(000) = 636$ ,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu = 61.2$  cm<sup>-1</sup>,  $D_x = 1.81$  g cm<sup>-3</sup>,  $R = 0.044$  for 2884 observed [ $I > 3\sigma(I)$ ] reflections. With respect to the pairs of Cl, N(py) and N(azo) atoms coordinating with Os, the isomer has an octahedral *cis-cis-cis* configuration. Relative shortness of Os–N(azo), 1.95 (1), 2.00 (1) Å, compared to Os–N(py), 2.02 (1), 2.05 (1) Å, together with long N=N distances, 1.28 (1), 1.33 (1) Å, indicate considerable  $\pi$ -backbonding power of the azo function.

**Introduction.** The azoimine chemistry of Os had remained a quite unexplored area until the synthesis, spectra and redox properties of dibromo- and dichlorobis[2-(*m*-tolyl)azopyridine]osmium(II) were reported by Ghosh, Goswami & Chakravorty (1983). Two isomers of the latter complex, blue–violet and red–violet in solution, have been isolated and characterized by spectral and chemical study. Dihalogenated metal complexes of 2-arylazopyridine may, in principle, occur in five different octahedral configurations. The coordinating pairs of halogen, N(py) and N(azo) atoms may be arranged *trans-trans-trans* (*ttt*), *trans-cis-cis* (*tcc*), *cis-trans-cis* (*ctc*), *cis-cis-trans* (*cct*) or *cis-cis-cis* (*ccc*). A structural study of the blue–violet isomer has already established its configuration to be *ctc* (Ghosh, Mukhopadhyay, Goswami, Ray & Chakravorty, 1984). The results also indicated the presence of strong Os–N(azo) bonding, similar to the Ru–N(azo) bonds in the 2-phenylazopyridine complexes of ruthenium (Seal & Ray, 1984). The present work was undertaken to determine the configuration of the coordination octahedron in the red–violet isomer, as well as to look for evidence, if any, of superior  $\pi$ -backbonding power of the azo function in this complex.

**Experimental.** Specimen size 0.3 × 0.2 × 0.15 mm. Nicolet Syntex R3 diffractometer, graphite-monochromated MoK $\alpha$  radiation. 15 reflections (to  $2\theta = 18.51^\circ$ ) for measurement of lattice parameters.  $D_m$  not measured since all suitable liquids available were solutions of bromides and iodides with which the crystal reacted;  $\omega$ – $2\theta$  scans,  $\theta_{\text{max}} = 25^\circ$ ,  $h$  0 to 10,  $k$  –12 to 12,  $l$  –15 to 15; 3946 unique reflections measured (no merging of equivalents), 1062 with  $I \leq 3\sigma(I)$  considered unobserved; 012 and 131 used as standards, intensities showed no decay throughout data collection; no absorption correction; structure solved by Patterson and successive Fourier syntheses. Least-squares refinement on  $F$ ; atomic scattering factors and  $f'$ ,  $f''$  for Os from *International Tables for X-ray Crystallography* (1974). Block diagonal approximation after the introduction of anisotropic thermal parameters. Towards the end of the refinement, the weighting scheme [ $w = 1/\sigma^2(F)$ ] was modified so as to reflect the trends in  $|\Delta F|$ , by adopting the following empirical values of  $\sigma(F)$  (Seal & Ray, 1981): for  $|F_o| \leq 14.7$ ,  $\sigma(F) = 0.282F_o$ ; for  $14.7 < |F_o| \leq 16.8$ ,  $\sigma(F) = 0.221F_o$ ; for  $16.8 < |F_o| \leq 18.6$ ,  $\sigma(F) = 0.196F_o$ ; for  $18.6 < |F_o| \leq 20.6$ ,  $\sigma(F) = 0.163F_o$ ; for  $20.6 < |F_o| \leq 22.8$ ,  $\sigma(F) = 0.133F_o$ ; for  $22.8 < |F_o| \leq 25.8$ ,  $\sigma(F) = 0.114F_o$ ; for  $25.8 < |F_o| \leq 29.4$ ,  $\sigma(F) = 0.091F_o$ ; for  $29.4 < |F_o| \leq 34.2$ ,  $\sigma(F) = 0.077F_o$ ; for  $34.2 < |F_o| \leq 44.3$ ,  $\sigma(F) = 0.068F_o$ ; for  $|F_o| > 44.3$ ,  $\sigma(F) = 0.063F_o$ . Sixteen H atoms kept fixed at their calculated positions; those belonging to the two CH<sub>3</sub> groups could not be located. Refinement converged [ $\text{max. } (\Delta/\sigma) = 0.459$ ] at  $R = 0.044$ ,  $wR = 0.051$ ,  $S = 1.004$ , for 2884 observed reflections. Final difference map showed max. and min. peaks of 0.8 and –0.8 e Å<sup>-3</sup>. All calculations carried out on a Burroughs 6700 computer; *XRAY ARC* program system (*World List of Crystallographic Computer Programs*, 1973) locally adapted for the B6700. Program sequence *NORMAL-EXFFT-SEARCH* from the *MULTAN78*

package (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) used for weighted Fourier synthesis.

**Discussion.** The refined positional parameters are in Table 1,\* and the distances and angles defining coordinating geometry in Table 2. A view of the molecule is shown in Fig. 1.

The complex has an octahedral *ccc* configuration. The coordination octahedron is greatly distorted,

\* Lists of structure factors, anisotropic thermal parameters, calculated H-atom coordinates, bond distances and angles in the ligands and equations of some mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43255 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters for non-hydrogen atoms with standard deviations in parentheses and equivalent isotropic temperature factors ( $\text{\AA}^2$ )

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	$B_{eq}$
Os	0.24631 (7)	0.28163 (5)	0.33609 (4)	2.5
Cl(1)	-0.0056 (4)	0.2561 (3)	0.2745 (2)	3.4
Cl(2)	0.1205 (4)	0.4956 (3)	0.3479 (2)	3.3
N(1)	0.182 (1)	0.1986 (9)	0.4740 (7)	2.8
N(2)	0.448 (1)	0.3268 (9)	0.3858 (7)	3.1
N(3)	0.327 (1)	0.097 (1)	0.3495 (7)	3.5
N(4)	0.330 (1)	0.359 (1)	0.2078 (7)	3.3
N(5)	0.450 (1)	0.420 (1)	0.2134 (8)	3.8
N(6)	0.292 (1)	0.0099 (9)	0.4186 (7)	3.4
C(1)	0.110 (2)	0.255 (1)	0.5456 (9)	3.4
C(2)	0.064 (2)	0.187 (1)	0.6323 (9)	3.9
C(3)	0.087 (2)	0.055 (1)	0.644 (1)	4.2
C(4)	0.163 (2)	-0.006 (1)	0.5761 (9)	3.9
C(5)	0.211 (2)	0.067 (1)	0.4892 (9)	3.6
C(6)	0.515 (2)	0.300 (1)	0.479 (1)	3.9
C(7)	0.647 (2)	0.348 (1)	0.502 (1)	4.2
C(8)	0.709 (2)	0.425 (2)	0.428 (1)	4.8
C(9)	0.647 (2)	0.452 (1)	0.330 (1)	4.5
C(10)	0.513 (1)	0.400 (1)	0.310 (1)	3.7
C(11)	0.268 (1)	0.376 (1)	0.1059 (8)	3.2
C(12)	0.281 (2)	0.484 (1)	0.034 (1)	4.3
C(13)	0.210 (2)	0.500 (2)	-0.059 (1)	5.5
C(14)	0.132 (2)	0.408 (2)	-0.083 (1)	5.7
C(15)	0.121 (2)	0.300 (1)	-0.014 (1)	4.4
C(16)	0.194 (1)	0.284 (1)	0.080 (1)	3.8
C(17)	0.374 (2)	-0.068 (1)	0.245 (1)	4.4
C(18)	0.459 (2)	-0.123 (1)	0.171 (1)	5.6
C(19)	0.577 (2)	-0.067 (2)	0.128 (1)	6.1
C(20)	0.619 (2)	0.033 (2)	0.156 (1)	5.8
C(21)	0.541 (2)	0.090 (1)	0.229 (1)	4.3
C(22)	0.420 (2)	0.038 (1)	0.2715 (8)	3.4
C(23)	0.032 (2)	0.202 (2)	-0.039 (1)	7.2
C(24)	0.412 (3)	-0.238 (2)	0.138 (2)	9.5

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in the coordination octahedron with e.s.d.'s in parentheses

Os—Cl(1)	2.382 (3)	Os—N(2)	2.019 (9)
Os—Cl(2)	2.385 (3)	Os—N(3)	1.95 (1)
Os—N(1)	2.051 (9)	Os—N(4)	2.00 (1)
Cl(1)—Os—Cl(2)	87.3 (1)	Cl(2)—Os—N(4)	87.1 (3)
Cl(1)—Os—N(1)	84.8 (3)	N(1)—Os—N(2)	97.2 (4)
Cl(1)—Os—N(2)	172.9 (3)	N(1)—Os—N(3)	74.7 (4)
Cl(1)—Os—N(3)	89.7 (3)	N(1)—Os—N(4)	174.5 (4)
Cl(1)—Os—N(4)	100.6 (3)	N(2)—Os—N(3)	97.4 (4)
Cl(2)—Os—N(1)	94.5 (3)	N(2)—Os—N(4)	77.6 (4)
Cl(2)—Os—N(2)	85.8 (3)	N(3)—Os—N(4)	103.9 (4)
Cl(2)—Os—N(3)	168.9 (3)		

mainly due to the chelate bite angle  $\sim 76^\circ$ , as in the case of the *ctc* isomer (Ghosh *et al.*, 1984).

Distances and angles in the chelate rings show a relatively long N—N distance [average 1.30  $\text{\AA}$ , compared, for example, to an average of 1.256  $\text{\AA}$  in the structure of 1-phenylazoacetaldehyde oxime (Roy & Sengupta, 1980)], and short Os—N(azo) bonds compared to the Os—N(py) bonds. A similar effect was also observed in the *ctc* isomer (Fig. 2). It is therefore reasonable to conclude that the inference made regarding the nature of the coordination in the *ctc* isomer, namely the major involvement of the azo function in  $\pi$  bonding which makes the net ( $\sigma + \pi$ ) bond order of Os—N(azo) larger, is valid also for the *ccc* isomer.

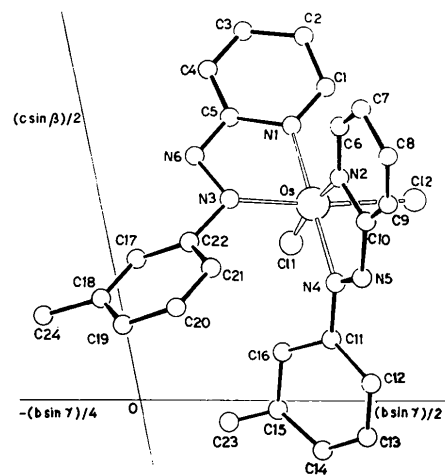


Fig. 1. The asymmetric unit of the structure viewed along a.

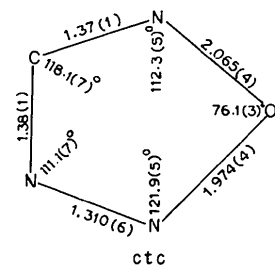
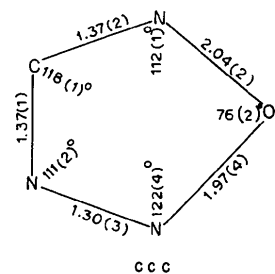


Fig. 2. Average distances ( $\text{\AA}$ ) and angles in the chelate rings of the *ccc* title complex and of the *ctc* isomer.

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## The Structure of Potassium Dihydroxyacetate (I) and Rubidium Dihydroxyacetate (II)

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**Abstract.** (I) K<sup>+</sup>.C<sub>2</sub>H<sub>3</sub>O<sub>4</sub><sup>-</sup>, *M<sub>r</sub>* = 130.1, monoclinic, *Pc*, *a* = 5.791 (4), *b* = 7.727 (6), *c* = 11.445 (6) Å, β = 120.00 (4)°, *V* = 443.5 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 1.92, *D<sub>x</sub>* = 1.95 Mg m<sup>-3</sup>, μ(Mo *Kα*, λ = 0.71069 Å) = 1.08 mm<sup>-1</sup>, *F*(000) = 264, *T* = 295 (2) K, final *R* = 0.036 for 2203 data including both *hkl* and *h̄k̄l* reflexions. (II) Rb<sup>+</sup>.C<sub>2</sub>H<sub>3</sub>O<sub>4</sub><sup>-</sup>, *M<sub>r</sub>* = 176.5, monoclinic, *P2<sub>1</sub>/c*, *a* = 5.665 (6), *b* = 12.846 (9), *c* = 6.391 (7) Å, β = 96.03 (7)°, *V* = 462.5 Å<sup>3</sup>, *Z* = 4, *D<sub>m</sub>* = 2.52, *D<sub>x</sub>* = 2.53 Mg m<sup>-3</sup>, μ(Mo *Kα*) = 11.2 mm<sup>-1</sup>, *F*(000) = 336, *T* = 300 (1) K, final *R* = 0.037 for 1239 non-zero reflexions. The X-ray analysis showed that potassium and rubidium glyoxylate crystallized from aqueous solutions exist in the solid state as salts of dihydroxyacetic acid. In the dihydroxyacetate anions different conformations about the C–C bond are observed. All O-bonded H atoms are involved in hydrogen bonds.

**Introduction.** In the biochemical literature glyoxylic acid is presented mostly as the simplest aldehydoacid, CHO–COOH. However, X-ray analysis (Lis, 1983) has shown that glyoxylic acid crystallizes from water as dihydroxyacetic acid CH(OH)<sub>2</sub>COOH. A similar result has been reported by Mattes & Uckelmann (1981) for the Na salt of this acid. Here are reported the crystal structures of potassium and rubidium salts of this acid.

**Experimental.** Potassium (rubidium) dihydroxyacetate was prepared by combining an equivalent quantity of glyoxylic acid monohydrate (Ferak Berlin) and

potassium (rubidium) carbonate in water. After slow evaporation of water many-faced, often twinned, crystals of (I) [rather irregular shaped crystals of (II)] appeared. *D<sub>m</sub>* measured pycnometrically in 1,2-dibromoethane/CCl<sub>4</sub> for (I) and in 1,2-dibromoethane/CHBr<sub>3</sub> for (II). Systematic absences on Weissenberg photographs uniquely indicated the space group for (II). For (I) the possible groups were *Pc* and *P2<sub>1</sub>/c*. Specimens 0.2 × 0.25 × 0.3 mm for (I) and 0.4 × 0.3 × 0.4 mm for (II) were cut from large crystals. Syntex *P2<sub>1</sub>* diffractometer, Mo *Kα* radiation for lattice parameters [15 reflexions, 20 ≤ 2θ ≤ 28° for (I) and 15 ≤ 2θ ≤ 34° for (II)] and intensity measurements; 2θ–ω scan technique. 2484 unique intensities below θ = 30° for (I) (*h* 0→8, *k* –10→10, *l* –15→13); 3051 reflexions below θ = 32.5° for (II) (*h* 0→8, *k* –19→19, *l* –9→9). After each group of 50 reflexions two standards were measured, variation ±5%. Most calculations performed on a Nova 1200 computer with locally modified *XTL/XTLE* (Syntex, 1976) programs. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); real and imaginary components of anomalous dispersion included for all non-H atoms. Both structures solved by the heavy-atom method. The K (Rb) atoms were found from a Patterson map. In the case of (I) the noncentrosymmetric space group *Pc* was assumed. All other atoms were found from difference maps. In each structure, refinement based on *F* (K, Rb, O, C anisotropic, H isotropic) for reflexions with *I* >