

The crystal structure projected along the *c** axis is illustrated in Fig. 1. The shortest distance between the anion and the cation is 3.54 (1) Å between atoms Cl(3) and C(25). The spatial orientation of the two independent cations is different; the dihedral angle between the coordination planes of cations 1 and 2 is 46.8°.

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Structure of Tris(dimethylglyoxime)ruthenium(II) Dichloride

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Abstract. (I) [Ru(C₄H₈N₂O₂)₃]Cl₂, *M_r* = 520, monoclinic, *C*2/*c*, *a* = 13.4890 (5), *b* = 9.6913 (7), *c* = 16.6847 (5) Å, β = 112.365 (3)°, *V* = 2017 (2) Å³, *Z* = 4, *D_x* = 1.71 g cm⁻³, λ(Cu *Kα*) = 1.5418 Å, μ = 93.2 cm⁻¹, *F*(000) = 1056, *T* = 295 (2) K, final *R* = 0.048 (*wR* = 0.053) for 1623 significant [|*F_{obs}*| ≥ 3σ(|*F_{obs}*|)] reflections. The molecule is propeller-like with three dimethylglyoxime-H₂ (dmgH₂) units bound to the Ru^{II} ion and occupies a special position (on a crystallographic twofold axis) in the unit cell. The Ru^{II} coordination is a distorted octahedron, Ru^{II}—N bonds [average 2.038 (4) Å] are even shorter than typical Ru^{III}—N distances (2.10 Å), implying considerable π bonding between the π* orbitals of dmg and the *t*_{2g} orbitals of Ru^{II}; the N—Ru—N bite angle (average) is 75.0 (2)°. The crystal structure is stabilized by intermolecular H bonding of the type O—H...Cl only and not by the intramolecular O—H...O interactions commonly observed in *trans*-bis(dmng) complexes.

Introduction. Although there is a wealth of literature available on *trans*-bis(dimethylglyoximate)metal

complexes (Chakravorty, 1974; Mariassy & Ondrejovic, 1990; Konno, Okamoto & Shirotani, 1989; Koman, Mariassy & Ondrejovic, 1991) along with a few *cis* isomers (Dwyer & Nyholm, 1946; Gillard & Wilkinson, 1963; Alcock, Atkins, Curzon, Golding & Sellars, 1980; Alcock, Atkins, Golding & Sellars, 1982), the tris(dimethylglyoxime)metal complexes are reported infrequently (Nakahara, Fujita & Tsuchida, 1956; Burger, Ruff & Ruff, 1965) and not characterized fully. A related example, whose X-ray structure is also reported, is the tris(oxamide oxime)-cobalt(III) complex (Bekaroglu, Sarisaban, Koray, Nuber, Weidenhammer, Weiss & Ziegler, 1978). This paper presents the first crystal structure of a tris(dimethylglyoxime) complex with ruthenium(II). Studies on ruthenium(II) complexes like the title compound (I) are carried out in our laboratory with the aim of understanding the underlying chemical and structural features responsible for the excited-state phenomena exhibited by these molecules, for example the tris(2,2'-bipyridyl)ruthenium(II) complex, a well known model compound for the photodissociation of water into oxygen and hydrogen (Rillema, Jones & Levy, 1979).

Experimental. Interaction of $[\text{Ru}^{\text{II}}(\text{dmsO})_4\text{Cl}_2]$ (Evans, Spencer & Wilkinson, 1973) with dmgH_2 (1:3 molar ratio) (dmsO = dimethyl sulfoxide, dmg = dimethylglyoxime) in refluxing methanol under inert atmosphere yielded the complex $[\text{Ru}^{\text{II}}(\text{dmgH}_2)_3]\text{Cl}_2$ (I) as a reddish brown crystalline solid. X-ray intensity data were collected in ω - 2θ scan mode from one of the suitable crystals ($0.18 \times 0.16 \times 0.05$ mm) on an Enraf-Nonius CAD-4 four-circle diffractometer with graphite-monochromatized $\text{Cu K}\alpha$ radiation. Unit-cell parameters were refined by least-squares method using 25 high-angle reflections. 3 control reflections monitored periodically for intensity decay and orientation remained constant within experimental error throughout data collection. The systematic absences (hkl , $h+k=2n$ and $h0l$, $l=2n$) indicated that the space group could be either Cc or $C2/c$. Max. $2\theta = 130^\circ$, $h = 0-15$, $k = 0-10$, $l = -19-19$. 1750 reflections measured, 1623 observed with $|F_o| \geq 3\sigma(|F_o|)$. Intensities were corrected for Lorentz and polarization effects and also empirically for absorption (North, Phillips & Mathews, 1968). For the latter, scans at intervals of 10° in ψ for 3 strong reflections selected near $\chi = 90^\circ$ served to evaluate the transmission ($0.28 \leq T \leq 1.00$). The $|E|$ -value statistics clearly showed a centric distribution favouring the choice of the space group $C2/c$ over Cc . This would imply that the molecule had a twofold axis coinciding with the crystallographic twofold axis. The Patterson map computed did give a special position (0.50, 0.16, 0.75) for the Ru atom. The structure was developed further by alternating rounds of Fourier synthesis and least-squares refinement on F . The full-matrix least-squares refinement of the 14 non-H atoms, isotropic followed by anisotropic, was carried out until convergence. The x and z coordinates of the Ru atom and the thermal parameters U_{12} and U_{23} were kept fixed throughout the LS refinement. The difference Fourier synthesis computed revealed all the H atoms at stereochemically reasonable positions. The final cycles of least-squares refinement with anisotropic non-H atoms and isotropic H atoms (kept fixed) using the modified unit weighting scheme (B. A. Frenz & Associates, Inc., 1985)* with the Dunitz-Seiler factor (Dunitz & Seiler, 1973) applied gave a final R index of 0.048 ($wR = 0.053$, $S = 0.94$). Reflection/parameter ratio = 13, $\Delta/\sigma < 0.03$, max. $|\Delta\rho|$ in the final difference map is $\sim 0.7 \text{ e } \text{\AA}^{-3}$. Scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV) and all the computations were carried out on a PDP-11/73 computer using *SDP* software (B. A. Frenz & Associates,

Inc., 1985). The final positional parameters of non-H atoms along with their equivalent isotropic thermal parameters are given in Table 1.†

Discussion. An *ORTEP* (Johnson, 1976) view of the molecule of the complex (I) is shown in Fig. 1, bond distances and angles in Table 2. The molecule has almost D_3 symmetry with three dmgH_2 units bound to the Ru^{II} metal centre in a propeller-like manner. However, the complex crystallizes in a monoclinic space group $C2/c$ with a crystallographic twofold axis passing through the centre of the $\text{C}(1)-\text{C}(1')$ bond and the Ru atom. The dihedral angles between the planes through the dmgH_2 chelate rings are unequal; the chelate ring $\text{Ru}-\text{N}(1)-\text{C}(1)-\text{C}(1')-\text{N}(1')$ through which the symmetry axis passes makes an angle of $98.0(1)^\circ$ with each of the other two dmgH_2 rings, the angle between the latter rings is only $93.0(1)^\circ$.

Ruthenium(II) coordination in (I) is a highly distorted octahedron. The $\text{N}-\text{Ru}-\text{N}$ bite angles of $74.8(2)^\circ$ [$\text{N}(1)-\text{Ru}-\text{N}(1')$] and $75.4(2)^\circ$ [$\text{N}(2)-\text{Ru}-\text{N}(3)$] are much reduced from the ideal octahedral value of 90° . The *trans* angles are less than 180° , $\text{N}(1)-\text{Ru}-\text{N}(2') = 170.7(2)^\circ$ and $\text{N}(3)-\text{Ru}-\text{N}(3') = 173.5(2)^\circ$. The $\text{N}-\text{Ru}-\text{N}$ bite angles in (I) are smaller than the value of $78.7(3)^\circ$ observed in the structure of tris(2,2'-bipyridyl) Ru^{II} (Rillema *et al.*, 1979) and much smaller than $81.6(3)^\circ$ observed in the tris(ethylenediamine) Ru^{II} complex (Smolenaers, Beattie & Hutchinson, 1981). *trans* distances $\text{Ru}^{\text{II}}-\text{N}(3)$ and $\text{Ru}^{\text{II}}-\text{N}(3')$ [$2.058(3) \text{ \AA}$] are slightly but significantly longer than the four equatorial $\text{Ru}^{\text{II}}-\text{N}$ distances [average $2.038(4) \text{ \AA}$]. Contrary to the expected increase resulting from larger ionic radius, $\text{Ru}^{\text{II}}-\text{N}$ bond distances in (I) are even shorter than $\text{Ru}^{\text{III}}-\text{N}$ bonds, for example $2.107(2) \text{ \AA}$ (average) observed in the crystal structure of $[\text{RuCl}(\text{NH}_3)_5]$ (Hambley, Keyte, Lay & Paddon-Row, 1991). The bond-length decrease suggests considerable π bonding between the t_{2g} orbitals of Ru^{II} and the π^* orbitals of dmgH_2 . The small difference between $\text{Ru}^{\text{II}}-\text{N}$ and $\text{Ru}^{\text{III}}-\text{N}$ bonds is recognized as one of the essential features of a complex having a higher rate of electron transfer between $[\text{RuL}]^{2+}$ and $[\text{RuL}]^{3+}$ (Rillema *et al.*, 1979; Smolenaers *et al.*, 1981); the lower rates on the other hand were also correlated with greater changes in $M-\text{N}$ bonds, for example in $\text{Co}(\text{NH}_3)_6^{2+}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ (Stynes & Ibers, 1971). It is noteworthy that $\text{Ru}^{\text{II}}-\text{N}$ distances

* Modified unit weighting scheme: $w = 1.0$ for $F_o < \text{THRES}$, $w = (\text{THRES}/F_o)^2$ for $F_o \geq \text{THRES}$, the default value of threshold THRES is 80% of the largest F_o . Available in program *WEIGHT* (B. A. Frenz & Associates, Inc., 1985).

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and intermolecular contacts $< 3.5 \text{ \AA}$ have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54988 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0033]

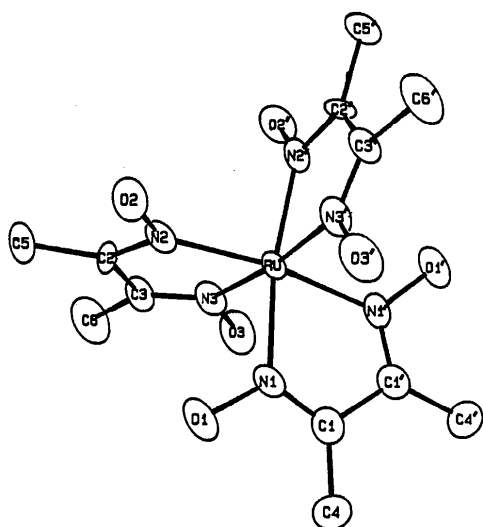
Table 1. Final positional parameters of non-H atoms and their *e.s.d.*'s

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2abc\cos\gamma)\beta_{12} + (2accos\beta)\beta_{13} + (2bccos\alpha)\beta_{23}]$$

	x	y	z	<i>B</i> _{eq} (Å ²)
Ru	0.500	0.16055 (5)	0.750	1.669 (6)
Cl	0.7373 (1)	-0.2165 (2)	0.82862 (8)	3.77 (3)
O(1)	0.5257 (3)	0.3189 (6)	0.6012 (2)	3.23 (7)
O(2)	0.5951 (3)	-0.0599 (5)	0.6670 (3)	3.45 (7)
O(3)	0.2594 (3)	0.2287 (6)	0.6573 (3)	3.79 (9)
N(1)	0.5159 (3)	0.3275 (5)	0.6816 (2)	2.28 (7)
N(2)	0.5065 (3)	0.0142 (5)	0.6647 (2)	2.32 (7)
N(3)	0.3457 (3)	0.1485 (5)	0.6595 (2)	2.62 (7)
C(1)	0.5066 (4)	0.4504 (6)	0.7077 (3)	2.73 (9)
C(2)	0.4199 (4)	-0.0098 (5)	0.5952 (3)	2.21 (7)
C(3)	0.3292 (3)	0.0720 (6)	0.5936 (3)	2.36 (8)
C(4)	0.5107 (6)	0.5795 (7)	0.6634 (4)	3.6 (1)
C(5)	0.4120 (6)	-0.1112 (7)	0.5262 (3)	3.6 (1)
C(6)	0.2214 (5)	0.060 (1)	0.5177 (4)	4.4 (1)

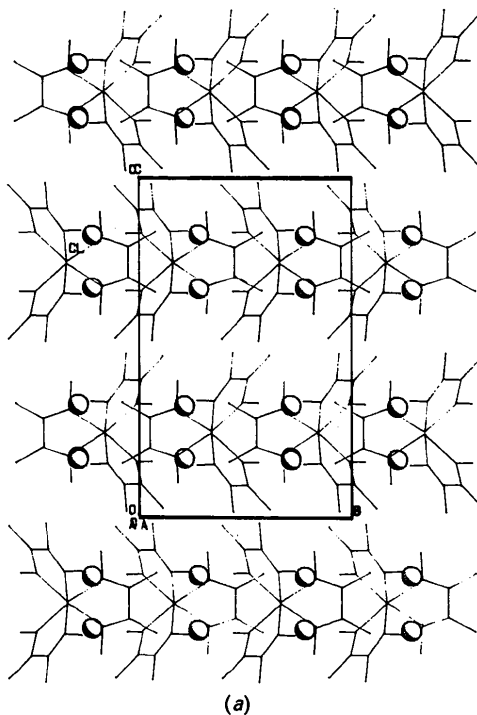
Table 2. Bond distances (Å) and bond angles (°) with *e.s.d.*'s in parentheses

Ru—N(1)	2.038 (4)	N(3)—C(3)	1.274 (6)
O(1)—N(1)	1.400 (5)	C(1)—C(1')	1.488 (8)
O(2)—N(2)	1.382 (6)	C(1)—C(4)	1.465 (9)
O(3)—N(3)	1.387 (7)	Ru—N(3)	2.058 (3)
N(1)—C(1)	1.290 (7)	C(2)—C(3)	1.450 (7)
Ru—N(2)	2.035 (4)	C(2)—C(5)	1.487 (7)
N(2)—C(2)	1.316 (5)	C(3)—C(6)	1.527 (6)
N(1)—Ru—N(1')	74.8 (2)	N(1)—C(1)—C(4)	126.3 (6)
N(1)—Ru—N(3')	85.8 (2)	C(1)—C(1)—C(4)	121.3 (5)
N(1')—Ru—N(2')	96.9 (2)	N(2)—C(2)—C(3)	112.4 (5)
N(2)—Ru—N(2')	91.7 (2)	N(2)—C(2)—C(5)	125.2 (5)
N(2)—Ru—N(3)	99.9 (2)	N(1)—Ru—N(2')	170.7 (2)
O(1)—N(1)—C(1)	115.8 (4)	N(1')—Ru—N(2)	170.7 (2)
O(2)—N(2)—C(2)	113.7 (5)	N(1')—Ru—N(3')	85.8 (2)
O(3)—N(3)—C(3)	115.7 (3)	N(2)—Ru—N(3')	99.9 (2)
N(1)—C(1)—C(1')	112.5 (5)	N(3)—Ru—N(3')	173.5 (5)
N(1)—Ru—N(2)	96.9 (2)	C(3)—C(2)—C(5)	122.4 (5)
N(1)—Ru—N(3')	99.4 (2)	N(3)—C(3)—C(2)	115.7 (3)
N(1')—Ru—N(3)	99.4 (2)	N(3)—C(3)—C(6)	123.9 (5)
N(2)—Ru—N(3)	75.4 (2)	C(2)—C(3)—C(6)	120.4 (5)
N(2')—Ru—N(3')	75.4 (2)		

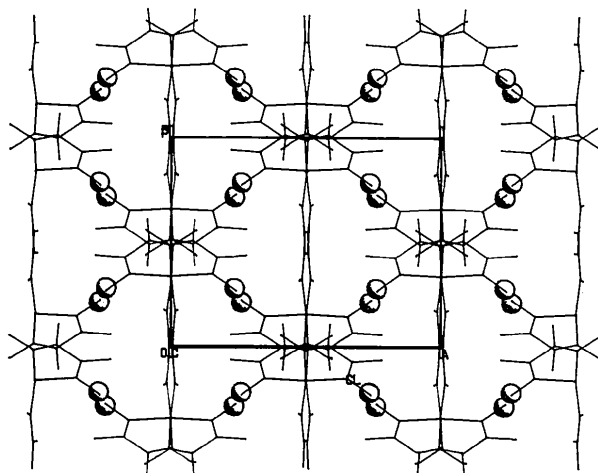
Fig. 1. ORTEP view of the molecule [Ru(dmgh₂)₃]²⁺. The primed atoms are twofold (crystallographically) related to the unprimed ones.

in (I) with the dmgh₂ ligand come very close to the value of 2.056 (6) Å observed in the tris(2,2'-bipyridyl)Ru^{II} complex (Rillema *et al.*, 1979).

The dmgh₂ rings are essentially planar; a small torsion angle of -2.6 (7)° is observed for N(2)—C(2)—C(3)—N(3) [and N(2')—C(2')—C(3')—N(3')] whereas torsion angle N(1)—C(1)—C(1')—N(1') is -6.0 (4)°. The bond distances and angles in independent dmgh₂ units bound to the metal ion show little variation, the bond C(3)—C(6) [1.527 (6) Å] is longer than the equivalent C(1)—C(4) [1.465 (9) Å] and



(a)



(b)

Fig. 2. Packing of molecules in the unit cell viewed (a) down the *a* axis and (b) down the *c* axis.

C(2)—C(5) [1.467 (7) Å] bonds. Atom C(6) shows the highest thermal anisotropy in the structure and perhaps a correction for this effect (not done here) may give a bond length closer to the other two.

The packing of the molecules viewed down the *a* and *c* axes is shown in Fig. 2. Intra- and intermolecular contacts show that there is no intramolecular H bonding between the hydroxyl groups of the dmgh₂ units but only a weak intermolecular H-bonding interaction of the type O—H...Cl [Cl...O(1) = 2.977 (4), Cl...O(2) = 3.053 (4), Cl...O(3) = 3.033 (5) Å] exists in the crystal lattice. Fig. 2 clearly depicts the interactions of chloride ions with the [Ru(dmgh₂)₃] cations *via* OH groups.

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Structure of *catena*-Poly[{tetrakis- μ -(acetato-*O*:*O'*)-dicopper(II)}- μ -{1,8-bis-(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane-*N*²,*N*^{2'}}]

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Abstract. Asymmetric unit $\text{Cu}(\text{bddo})_{0.5}(\text{acetate})_2 = 0.5[\text{Cu}_2(\text{C}_{16}\text{H}_{26}\text{N}_4\text{S}_2)(\text{C}_2\text{H}_3\text{OO})_4]$, $M_r = 350.90$, triclinic, $P\bar{1}$, $a = 8.501$ (1), $b = 8.590$ (1), $c = 10.854$ (2) Å, $\alpha = 84.54$ (2), $\beta = 82.10$ (2), $\gamma = 84.73$ (2)°, $V = 779$ Å³, $Z = 2$, $D_x = 1.49$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 15.4$ cm⁻¹, $F(000) = 364$, $T = 298$ K, $R = 0.041$ and $wR = 0.047$ for 1648 unique reflections [$I > 2\sigma(I)$]. The structure of this new compound consists of dinuclear $\text{Cu}_2(\text{CH}_3\text{COO})_4$

units linked to a chain by the ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) along the body diagonal of the unit cell. The Cu atoms are coordinated by four O atoms from the acetates and one N atom from the ligand bddo in a square pyramidal geometry with the pyrazole N atom in the apical position. In the copper acetate dimer the basal planes of two square pyramids are facing each other. The Cu—O(acetate) distances in the dinuclear copper acetate unit can be regarded as normal, as well as the Cu—N(bddo) distances. The Cu—Cu

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