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# Silver 2-Pyrimidinolate Dihydrate, [$Ag(C_4H_3N_2O)$].$2H_2O$: a Case of Pseudosymmetry

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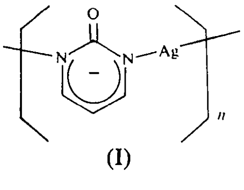
## Abstract

The title compound, *catena*-poly[silver-$\mu$-(2-pyrimidinolato-$N$:$N'$) dihydrate], exhibits a case of pseudosymmetry, the supergroup being *Aema* (*Cmce* in standard setting) and the subgroup *Pbca*, identified *a posteriori* by trial and error. A considerable extinction effect is present, making the space-group assignment more difficult. The structure consists of infinite chains along the *b* axis, with alternating Ag atoms and 2-pyrimidinolate ligands. Each metal atom is placed at a false symmetry centre and is linearly coordinated by one N atom of each of two ligands. A false mirror plane passes through the middle of the organic moiety, which is attached to two Ag atoms *via* its two N atoms. The chains are linked by the water molecules, which are hydrogen bonded to one another and to the carbonyl O atoms, and also by direct Ag···Ag interactions.

## Comment

Continuing our structural studies on metal derivatives of 2-pyrimidinol (Quirós & Enrique, 1993), silver 2-pyrimidinolate, (I), was synthesized and its structure determined by X-ray diffraction. The result was an interesting example of apparent symmetry higher than real symmetry.



(I)

Pseudosymmetry is a rather frequent problem in crystallography, when there appears to be a space group (supergroup) with higher symmetry than the real group. The best known examples of this are in quasi-centrosymmetrical crystals (Tadini, 1981; Quirós, Salas, Sánchez, Beauchamp & Solans, 1993) and subcells.

The structure reported here shows an example of pseudosymmetry: the supergroup is *Aema** [new symbol for this space group according to the rules proposed by de Wolff *et al.* (1992)] and the real group could be any of its eight centrosymmetric orthorhombic subgroups, the overall features of the structure being readily identified in any of the nine. The intensity distribution is rather peculiar, with the 'even *h* and even *k* and even *l*' reflections 80 times stronger than the 'odd *h* or odd *k* or odd *l*'. This, together with the possible Renninger effects associated with the considerable extinction suffered by the 'three even index' reflections, made it difficult to assign *a priori* the real space group.

The structure comprises endless chains along the *b* axis, in which Ag atoms and deprotonated 2-pyrimidinol molecules alternate. The position of the Ag atom corresponds with a pseudo-inversion centre in the structure, being linearly coordinated by N(1) of one ligand and N(3) of another. The organic moiety is bisected by the pseudo-mirror plane at $y = 0$, being attached to two metal atoms *via* its two N atoms. Fig. 1(*a*) shows the asymmetric (but pseudosymmetric) unit and Fig. 1(*b*) displays a view of the polymer.

The coordination geometry around the Ag atom is virtually linear, with Ag—N distances comparable to those in complexes such as $[Ag(NH_3)_2]^+$ (Zachwieja & Jacobs, 1992). Distances to the O atoms in the ligands and in the water molecules are long enough [the shortest is Ag···O(1*W*) 3.136 (3) Å] to neglect any possible interaction. The contact with the other two Ag atoms placed above and below in the [100] direction at 3.302 (1) Å, which generates Ag rows along the *a* axis (see Fig. 2), is perhaps more significant. Much shorter Ag···Ag distances (2.7–3.1 Å) have been observed for dimeric compounds of this metal (Cotton, Feng, Matusz & Poli, 1988; Tiekink, 1990; Chen & Mak, 1991), though in these cases the actual value seems to be conditioned by the presence of a ligand which simultaneously binds the two atoms.

Bond distances within the ligand (see Table 3) are similar to those it presents when it is free (Furberg & Solbakk, 1970) or coordinated in neutral [N(1) protonated] forms (Cartwright, Reynolds & Skapski, 1977; Quirós & Enrique, 1993), with only random differences below 0.03 Å being observed. C(2)—O(2) in particular clearly remains a double bond. On the other hand, changes in bond angles are more significant, owing to the increased symmetry, with the endocyclic angles at N(1) (−4°) and C(6) (+4°) the most outstanding. Angle distortion towards higher

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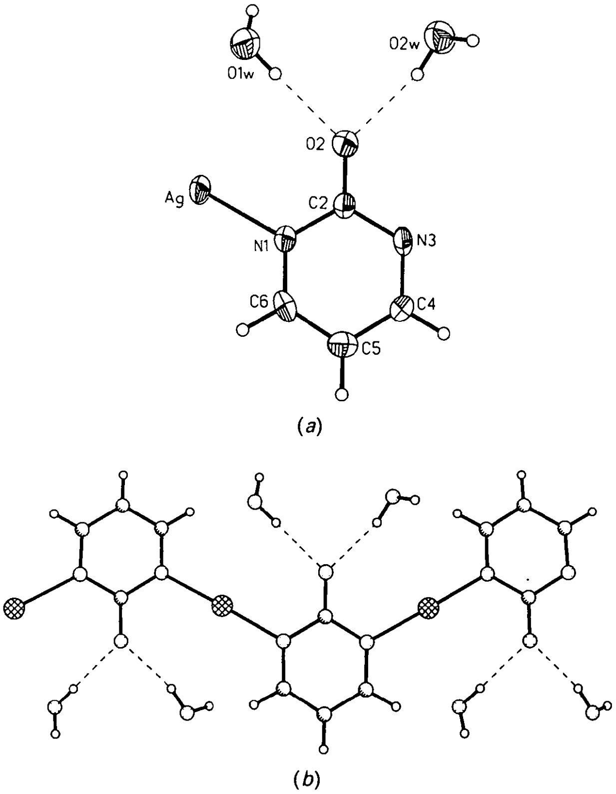
* Non-standard settings are used for several spaces groups throughout the paper. This avoids changes in orientation that would be very confusing for the reader.



(a)

(b)

Fig. 1. (a) Asymmetric unit of the title compound, with atoms represented as 50% probability ellipsoids. (b) Three units of one of the polymeric chains that grow along the b axis.

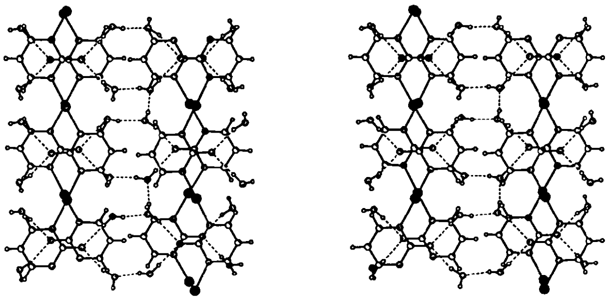


Fig. 2. Stereoview of the packing down the a axis (b vertical and c horizontal). The hydrogen-bond network between the chains is shown.

symmetry is also displayed by the 2-hydroxypyrimidinium cation (Furberg & Aas, 1975) though the reason for it is just the opposite [protonation at N(3) instead of deprotonation at N(1)]. The carbonyl O atom is placed noticeably out [0.243 (3) Å] of the average plane of ring atoms, this being attributed to the interaction with water molecules. The two coordinated Ag atoms are displaced 0.357 (1) and 0.367 (1) Å out of this plane.

Fig. 2 displays how the polymer chains are packed to build the structure. Each water molecule is hydrogen bonded to one carbonyl O atom and to two other water molecules, joining in this way every chain with its neighbours in the [001] and [101] directions. Hexagons are formed by hydrogen-bonded O atoms around true inversion centres of the crystal. Chains are stacked along the a axis with metal atoms forming rows as described above and pyrimidine rings alternating on both sides of the $z = 0$ plane.

## Experimental

The compound was obtained by mixing solutions (ca 50 $\text{cm}^3$ each) of 1 mmol $AgNO_3$ and 1 mmol 2-pyrimidinol in 1M ammonia. The solution was allowed to stand for 24 h to allow excess ammonia to evaporate off.

*Crystal data*

$[Ag(C_4H_3N_2O)].2H_2O$
$M_r = 239.0$
Orthorhombic
*Pbca*
$a = 6.603\ (1)$ Å
$b = 11.933\ (2)$ Å
$c = 16.743\ (3)$ Å
$V = 1319.2\ (4)$ Å$^3$
$Z = 8$
$D_x = 2.406$ Mg m$^{-3}$
$D_m = 2.41$ Mg m$^{-3}$
$D_m$ measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 15\text{–}22°$
$\mu = 2.972$ mm$^{-1}$
$T = 293$ K
Brick-shaped prisms
0.37 × 0.18 × 0.10 mm
Colourless

*Data collection*

Siemens *R*3*m*/*V* diffractometer
$\omega$ scans
Absorption correction: numerical
$T_{\min} = 0.588$, $T_{\max} = 0.746$
1784 measured reflections
1515 independent reflections
892 observed reflections
$[F > 4\sigma(F)]$

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 21$
3 standard reflections
frequency: 90 min
intensity variation: ±3%

*Refinement*

Refinement on $F$
$R = 0.034$
$wR = 0.064$
$S = 0.87$
892 reflections
106 parameters
$w = 1/[\sigma^2(F) + 0.004F^2]$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.91$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.34$ e Å$^{-3}$
Extinction correction: Larson (1970)
Extinction coefficient: 0.051 (4)
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1987)

Table 1. *Intensity distribution of the diffraction data*

| Group of reflections | $N$* | $I > 3\sigma(I)$ | $\langle I \rangle$† |
|---|---|---|---|
| All | 1784 | 825 | 304.6 |
| Even *h* and even *k* and even *l* | 256 | 256 | 1970.9 |
| Odd *h* or odd *k* or odd *l* | 1528 | 569 | 24.3 |
| Odd $h + k$ | 893 | 232 | 24.3 |
| Odd $h + l$ | 890 | 426 | 30.1 |
| Odd $k + l$ | 893 | 252 | 7.5 |
| Even $k + l$, with at least one odd index | 635 | 317 | 48.1 |
| *hk*0, odd *h* | 53 | 1 | 1.3 |
| *hk*0, odd *k* | 57 | 7 | 2.3 |
| *hk*0, odd $h + k$ | 60 | 8 | 2.5 |
| *h*0*l*, odd *h* | 74 | 24 | 31.9 |
| *h*0*l*, odd *l* | 79 | 7 | 2.3 |
| *h*0*l*, odd $h + l$ | 81 | 29 | 30.4 |
| 0*kl*, odd *k* | 137 | 13 | 2.1 |
| 0*kl*, odd *l* | 139 | 52 | 8.5 |
| 0*kl*, odd $k + l$ | 140 | 53 | 8.3 |
| *h*00, odd *h* | 4 | 1 | 2.5 |
| 0*k*0, odd *k* | 8 | 3 | 5.8 |
| 00*l*, odd *l* | 10 | 6 | 9.7 |

* *N* is the total number of reflections collected.

† $\langle I \rangle$ is the average intensity (in arbitrary units) of the group.

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| Ag | 0.00063 (6) | 0.24848 (2) | 0.24795 (2) | 0.0325 (3) |
| N(1) | 0.0854 (4) | 0.0987 (2) | 0.3065 (2) | 0.028 (1) |
| C(2) | 0.0775 (6) | −0.0015 (2) | 0.2664 (2) | 0.025 (1) |
| O(2) | 0.0613 (5) | −0.0029 (2) | 0.1922 (2) | 0.038 (1) |
| N(3) | 0.0851 (4) | −0.1002 (2) | 0.3087 (2) | 0.027 (1) |
| C(4) | 0.1308 (6) | −0.0968 (3) | 0.3862 (2) | 0.029 (1) |
| C(5) | 0.1639 (6) | 0.0017 (3) | 0.4266 (2) | 0.032 (1) |
| C(6) | 0.1288 (6) | 0.0981 (3) | 0.3843 (2) | 0.031 (1) |
| O(1*W*) | 0.1211 (5) | 0.1656 (2) | 0.0767 (2) | 0.047 (1) |
| O(2*W*) | 0.0990 (5) | −0.1615 (3) | 0.0671 (2) | 0.047 (1) |

Table 3. *Selected geometric parameters* (Å, °)

| | | | |
|---|---|---|---|
| Ag—N(1) | 2.114 (3) | C(2)—N(3) | 1.375 (4) |
| Ag—N($3^{\rm i}$) | 2.117 (3) | N(3)—C(4) | 1.333 (5) |
| N(1)—C(2) | 1.372 (4) | C(4)—C(5) | 1.373 (5) |
| N(1)—C(6) | 1.333 (5) | C(5)—C(6) | 1.371 (5) |
| C(2)—O(2) | 1.249 (5) | | |
| N(1)—Ag—N($3^{\rm i}$) | 179.0 (1) | C(2)—N(3)—C(4) | 118.9 (3) |
| Ag—N(1)—C(2) | 120.0 (2) | C(2)—N(3)—$\rm Ag^{ii}$ | 119.3 (2) |
| Ag—N(1)—C(6) | 121.0 (2) | C(4)—N(3)—$\rm Ag^{ii}$ | 121.5 (2) |
| C(2)—N(1)—C(6) | 118.7 (3) | N(3)—C(4)—C(5) | 122.8 (3) |
| N(1)—C(2)—O(2) | 120.2 (3) | C(4)—C(5)—C(6) | 115.9 (3) |
| N(1)—C(2)—N(3) | 119.5 (3) | N(1)—C(6)—C(5) | 123.1 (3) |
| O(2)—C(2)—N(3) | 120.3 (3) | | |

| $D$ | H | $A$ | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|---|
| O(1*W*) | H(12*W*) | O(2) | 1.99 (4) | 2.817 (4) | 172 (5) |
| O(1*W*) | H(11*W*) | O($2W^{\rm iii}$) | 1.99 (3) | 2.813 (4) | 171 (5) |
| O(2*W*) | H(22*W*) | O(2) | 2.00 (4) | 2.833 (4) | 165 (4) |
| O(2*W*) | H(21*W*) | O($1W^{\rm iv}$) | 1.92 (4) | 2.775 (5) | 168 (4) |

Symmetry codes: (i) $-x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-x, -y, -z$; (iv) $\frac{1}{2} - x, -\frac{1}{2} + y, z$.

Table 1 shows the distribution of the intensity data. There is a remarkable periodicity along the three axes, reflections with three even indices being about 80 times stronger than those with one or more odd indexes. Reflections with odd $k + l$ are extremely weak, more than six times weaker than the rest with at least one odd index, which indicates that the structure is probably almost *A* centred, though the number of these reflections with $I > 3\sigma(I)$ (28%) is enough to assign the cell as primitive. A close examination of Weissenberg photographs confirmed this, indicating that an *A*-centred supergroup, easily identified as *Aema*, is present.

The analysis of Table 1 is far from being conclusive for an unequivocal identification of the subgroup, especially because appreciable Renninger effects are likely to be present: it is clear from the refinement process that the very intense 'even *h*, even *k*, even *l*' reflections are considerably affected by extinction, and extinction and Renninger effects are correlated. So, a complete structure solution and refinement process was carried out in the eight orthorhombic centrosymmetric subgroups of *Aema* (*Pbma*, *Pbcn*, *Pcmn*, *Pcca*, *Pbmn*, *Pbca*, *Pcma* and *Pccn*) in order to identify the best solution *a posteriori*. Ag atoms were placed on all inversion centres in the former four groups and in the general position $(0,\frac{1}{4},\frac{1}{4})$ in the latter four. Reflections with $F > 4\sigma(F)$ were considered as observed in all cases.

The results obtained in *Pbca* were clearly better than those obtained in the other seven groups. Unacceptable displacement parameters thus appeared for some of the atoms in all except the *Pbca* space group. Also, H atoms were clearly identified (with water H atoms in the expected position for hydrogen bonding) in this space group but not in the others. H atoms of 2-pyrimidinolate, however, were idealized while those of water were refined with fixed O—H (0.85 Å) and H···H (1.35 Å) distances. In all cases it was important to introduce an empirical isotropic extinction parameter in order to carry out the refinement: $\chi = 0.0051$ (4) in *Pbca* (very close to the value in the other cases).

In *Pbca* the final values of *R*, *wR* and *S* were 0.034, 0.064 and 0.87, respectively; in the other groups these parameters were in the ranges 0.06–0.08, 0.20–0.26 and 2.9–3.7, respectively. The strongest difference peak and hole (both near the Ag atom) in the final map were 0.91 and $-1.34$ e Å$^{-3}$ in *Pbca*. In the other space groups the values ranged from ±1.2 to ±3.3 e Å$^{-3}$. $(\Delta/\sigma)_{\rm max}$ was less than 0.001 in all cases.

In order to check if the inconsistencies for *Pbca* displayed in Table 1 (especially those gathered together along the *c* axis) may be really assignable to Renninger effects, a second crystal was mounted and the reflections *h*00, 0*k*0 and 00*l* with the non-zero index odd were measured at different $\psi$ angles. Negligible intensities were obtained in all cases. A few 'odd $k + l$' reflections were also measured to recheck the primitive cell and, thus, definitively reject the supergroup.

The solution in *Pbca* was then assumed to be correct and final refined coordinates of non-H atoms in this space group are listed in Table 2.

The *SHELXTL-Plus* (Sheldrick, 1987) package, on a MicroVAXII computer, was used for calculations and drawings.

The author is grateful to Dr David Williams, X-ray Crystallography Laboratory, Imperial College of Science and Technology and Medicine, London, for collecting the diffraction data.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1029). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# Bis(dimethylglyoximato-*N*,*N'*)(ethyl)(triphenylphosphine)rhodium(III)

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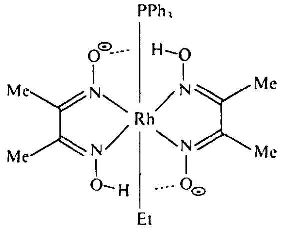
## Abstract

The structure of $[Rh(C_4H_7N_2O_2)_2(C_2H_5)(C_{18}H_{15}P)]$ consists of discrete complex molecules in which the Rh atom displays distorted octahedral coordination; the two dimethylglyoxime ligands lie in the equatorial plane and the ethyl and triphenylphosphine groups occupy the axial positions. The Rh atom is displaced by 0.130(1) Å from the mean plane through the four oxime N donor atoms in the direction of the P atom. The Rh—N distances range from 1.903 (6) to 1.993 (6) Å, while the axial Rh—P and Rh—C distances are 2.461 (2) and 2.064 (7) Å, respectively. Comparison of the results with those obtained previously for analogous compounds containing the axial fragment $Ph_3P—Rh—X$ indicates that the *trans* influence of *X* is determined by its σ-donor power.

## Comment

This work is part of a more general study aimed at understanding the mutual electronic influences of ligands in organometallic compounds (Steinborn, 1992). The *trans* influence of σ-organo ligands is of particular interest. In this paper we report the crystal structure of $[Rh(dmgH)_2(PPh_3)Et]$ (dmgH = monoanion of dimethylglyoxime), (I). The molecular structure and the numbering scheme are shown in Fig. 1.



(I)

The complex crystallizes with discrete molecules, in which the Rh atom exhibits a distorted octahedral stereochemistry, with four oxime N donor atoms in the equatorial positions. The two dimethylglyoxime ligands are stabilized by two intramolecular hydrogen bonds acting between O(1) and O(4) [O···O = 2.560 (7) Å] and between O(2) and O(3) [O···O = 2.671 (7) Å]. Although the H atoms were not located from the Δρ map, on the basis of the oxime N—O distances (Table 2) it appears that the protons are more tightly bonded to O(4) and O(2) than to O(1) and O(3). In this respect the title structure agrees with those of analogous complexes which have pyridine as the axial base, $[Rh(dmgH)_2(py)R]$ (Bresciani Pahor, Dreos-Garlatti, Geremia, Randaccio, Tauzher & Zangrando, 1990; Randaccio, Geremia, Dreos-Garlatti, Tauzher, Asaro & Pellizer, 1992).

The Rh—N bond distances range from 1.903 (6) to 1.993 (6) Å. These values are slightly shorter than those in the closely related complex $[Rh(dmgH)_2$-