

The Structure of Tetrakis(acetato)bis(4-pyridinecarbonitrile)dirhodium(II) Acetonitrile Solvate, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{C}_6\text{H}_4\text{N}_2)_2]\cdot\text{CH}_3\text{CN}$

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Abstract. $M_r = 691.27$, monoclinic, space group $P2_1/c$, $a = 8.385$ (2), $b = 12.024$ (4), $c = 26.132$ (3) Å, $\beta = 97.15$ (2)°, $V = 2614$ (2) Å³, $Z = 4$, $D_x = 1.756$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu(\text{Mo } K\alpha) = 12.846$ cm⁻¹, $F(000) = 1376$, $T = 299$ K. The structure of the title compound was solved using a combination of direct methods, difference Fourier, and least-squares refinement techniques with 3666 unique reflections of which 3098 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used to give final residuals of $R = 0.030$ and $R_w = 0.046$. The asymmetric unit consists of two Rh atoms connected by a bond of length 2.393 (1) Å, four acetate ligands symmetrically bridging the Rh–Rh bond, two 4-pyridinecarbonitrile ligands axially coordinated through the heterocyclic N atoms at 2.244 (4) and 2.243 (4) Å from each Rh atom, and a molecule of acetonitrile that occupies a general position in the crystal lattice.

Introduction. Nitrogen donor adducts of tetrakis(carboxylato)dirhodium(II) compounds constitute the largest class of $\text{Rh}_2(\text{O}_2\text{CR})_4L_2$ compounds studied (Cotton & Walton, 1982; Felthouse, 1982). Although a preliminary analysis of the structural data (Koh & Christoph, 1978) suggested a linear correlation between the Rh–Rh distance and the $\text{p}K_b$ of the nitrogen donor adduct, examination of a wider range of $\text{Rh}_2(\text{O}_2\text{CR})_4L_2$ structures suggests that a simple correlation between the Rh–Rh bond length and the basicity of the axial ligand does not exist (Cotton & Felthouse, 1981). For example, in going from $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(\text{pyridine})_2$ (Koh & Christoph, 1978) to $\text{Rh}_2(\text{O}_2\text{CC}_2\text{H}_5)_4(\text{acridine})_2$ (Cotton & Felthouse, 1981), not only do the Rh–Rh bond lengths increase from 2.3963 (2) to 2.417 (1) Å, but the Rh–N distances *also increase* from a value of 2.227 (3) Å in the pyridine adduct to 2.413 (3) Å for the acridine complex. These changes in bond lengths are opposite to that expected for *trans*-effect influences across the Rh–Rh bond.

Previous structural work has found that 1:1 adducts form between $\text{Rh}_2(\text{O}_2\text{CR})_4$ and an excess of bifunctional ligands such as phenazine or durenediamine (Cotton & Felthouse, 1981) in which the donor atom

groups are identical. Despite initial observations to the contrary (Das, Kadish & Bear, 1978), various nitrile adducts with $\text{Rh}_2(\text{O}_2\text{CR})_4$ have been isolated as crystalline compounds (Cotton & Thompson, 1981; Christoph, Koh & Kountz, 1982; Cotton & Thompson, 1983) establishing the stability of the Rh–nitrile nitrogen bond. With the above information in mind, a structural study was undertaken on the crystalline product formed between $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ and excess 4-pyridinecarbonitrile (4-CN-py), a molecule that contains both heterocyclic N and nitrile N atoms. This report presents the results of that study.

Experimental. Anhydrous rhodium(II) acetate was prepared by a literature method (Rempel, Legzdins, Smith & Wilkinson, 1972) using hydrated rhodium trichloride (Johnson Matthey, Inc.). To a suspension of 0.05 g (0.11 mmol) of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ in 10 ml of benzene was added 0.10 g (0.96 mmol) of 4-CN-py (Aldrich). The mixture produced an orange solution upon addition of 10 ml of acetonitrile. Evaporation of this solution to *ca* 2 ml total volume produced reddish-orange prismatic crystals. A very few red crystals were observed, but these were too small to investigate further.

Crystal 0.20 × 0.25 × 0.45 mm attached to a glass fiber with epoxy cement, Syntex $P\bar{1}$ autodiffractometer, arbitrary orientation along the long crystal dimension; 15 intense reflections ($25^\circ < 2\theta < 28^\circ$) centered and setting angles used as input for an autoindexing program, monoclinic cell chosen from which an orientation matrix was calculated for use in data collection; unit-cell parameters from a least-squares fitting of the setting angles for 25 reflections ($24^\circ < 2\theta < 37^\circ$) on an Enraf–Nonius CAD-4F diffractometer, data collected on the Syntex $P\bar{1}$ diffractometer, θ – 2θ scans, graphite-monochromated Mo $K\alpha$ radiation, variable scan rate 2.0 to 24.0° min⁻¹ with a symmetric scan range from $2\theta(\text{Mo } K\alpha_1) - 0.8^\circ$ to $2\theta(\text{Mo } K\alpha_2) + 0.8^\circ$, $2\theta_{\text{max}} = 50^\circ$ ($+h, +k, \pm l$), 3666 unique reflections, 3098 of which having $F_o^2 > 3\sigma(F_o^2)$ used in the refinement; three reflections ($17\bar{5}, 1, 3, 14$ and $52\bar{5}$) monitored every 97 reflections showed an average decline in I of 1.1% over the 38.7 h of X-ray exposure

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time, but this was not significant compared to the standard deviations of the intensities based on counting statistics alone; corrections for Lorentz and polarization effects but not absorption. Direct methods [*MULTAN* (Germain, Main & Woolfson, 1971)] for the two independent Rh atoms, least-squares refinement followed by difference Fourier maps for the remaining 35 atoms; 37 non-hydrogen atoms anisotropic, structure refined to near convergence when intensities of several low-angle reflections suggested the need for a secondary extinction correction: $|F_o| = |F_c|(1 + gI_c)^{-1}$, g from least-squares refinement = 3.19×10^{-8} ; for 335 variable parameters final $R_1 = 0.030$ and $R_w = 0.046$, $w = 4F_o^2/\sigma(F_o^2)^2$; $S = 1.117$, $(\Delta/\sigma)_{\max} = 0.02$, final maximum $\Delta\rho$ excursion $0.32 \text{ e } \text{\AA}^{-3}$ (associated with an H-atom position); all 23 H atoms located in the top 40 difference Fourier peaks, but no attempt made to include them in the refinement; PDP 11/45 or PDP 11/60 computers at the Molecular Structure Corporation, College Station, Texas; Enraf-Nonius (1981) *Structure Determination Package* with local modifications.

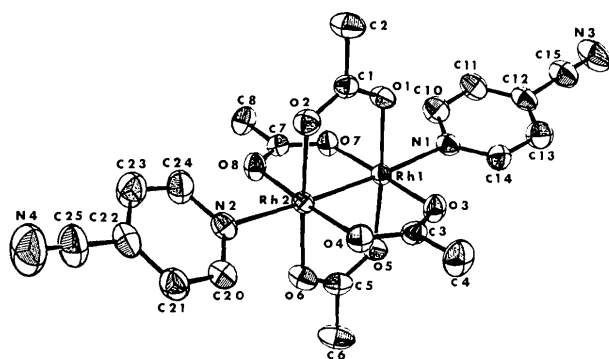


Fig. 1. ORTEP drawing (Johnson, 1965) of the dirhodium complex in $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(4\text{-CN-py})_2 \cdot \text{CH}_3\text{CN}$ with thermal ellipsoids shown at the 50% probability level.

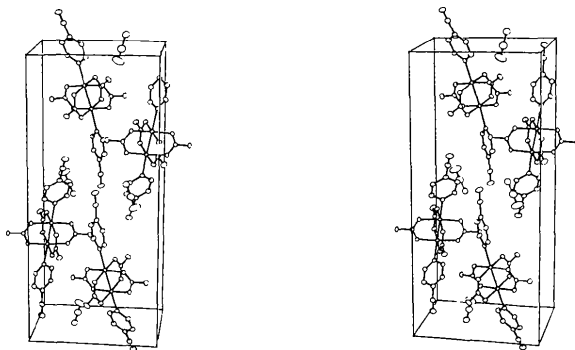


Fig. 2. Stereoscopic view of the unit-cell contents of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(4\text{-CN-py})_2 \cdot \text{CH}_3\text{CN}$ along the a axis with the b axis horizontal and the c axis vertical. Vibrational ellipsoids enclose 20% of their electron density. The origin is located in the left upper rear corner.

Table 1. Positional parameters and equivalent isotropic thermal parameters for $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(4\text{-CN-py})_2 \cdot \text{CH}_3\text{CN}$, with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B(\text{\AA}^2)$
Rh(1)	0.41653 (4)	0.61371 (3)	0.86349 (1)	2.031 (7)
Rh(2)	0.33413 (4)	0.56941 (3)	0.77485 (1)	2.099 (7)
O(1)	0.6247 (4)	0.6765 (3)	0.8413 (1)	2.83 (8)
O(2)	0.5477 (4)	0.6314 (3)	0.7588 (1)	2.92 (8)
O(3)	0.3128 (4)	0.7668 (3)	0.8506 (1)	2.98 (8)
O(4)	0.2319 (4)	0.7239 (3)	0.7673 (1)	2.87 (7)
O(5)	0.2022 (4)	0.5483 (3)	0.8791 (1)	2.94 (8)
O(6)	0.1254 (4)	0.5065 (3)	0.7957 (1)	3.20 (8)
O(7)	0.5162 (4)	0.4603 (3)	0.8713 (1)	2.68 (7)
O(8)	0.4440 (4)	0.4196 (3)	0.7878 (1)	2.91 (8)
N(1)	0.5075 (5)	0.6522 (4)	0.9460 (2)	2.70 (9)
N(2)	0.2698 (5)	0.5297 (4)	0.6909 (2)	2.60 (9)
N(3)	0.7997 (7)	0.7716 (6)	1.1315 (2)	5.8 (2)
N(4)	0.2131 (8)	0.5012 (6)	0.4861 (2)	6.7 (2)
N(100)	0.107 (1)	0.685 (1)	0.0232 (4)	13.8 (4)
C(1)	0.6472 (6)	0.6719 (4)	0.7942 (2)	2.4 (1)
C(2)	0.8006 (7)	0.7195 (6)	0.7790 (2)	3.7 (1)
C(3)	0.2453 (6)	0.7892 (4)	0.8058 (2)	2.6 (1)
C(4)	0.1772 (8)	0.9051 (5)	0.7970 (3)	4.2 (1)
C(5)	0.1055 (6)	0.5086 (5)	0.8424 (2)	3.0 (1)
C(6)	-0.0531 (7)	0.4616 (6)	0.8566 (3)	4.6 (1)
C(7)	0.5102 (6)	0.3967 (4)	0.8323 (2)	2.5 (1)
C(8)	0.5926 (7)	0.2855 (5)	0.8405 (2)	3.4 (1)
C(10)	0.6195 (7)	0.5853 (5)	0.9712 (2)	3.8 (1)
C(11)	0.6964 (7)	0.6113 (5)	1.0202 (2)	3.8 (1)
C(12)	0.6544 (7)	0.7082 (5)	1.0432 (2)	3.4 (1)
C(13)	0.5368 (7)	0.7779 (6)	1.0177 (2)	4.0 (1)
C(14)	0.4662 (7)	0.7444 (5)	0.9692 (2)	3.3 (1)
C(15)	0.7364 (7)	0.7423 (6)	1.0929 (2)	4.3 (1)
C(20)	0.1434 (6)	0.5776 (5)	0.6617 (2)	3.0 (1)
C(21)	0.1224 (7)	0.5688 (5)	0.6091 (2)	3.3 (1)
C(22)	0.2347 (7)	0.5116 (5)	0.5850 (2)	3.5 (1)
C(23)	0.3662 (8)	0.4604 (6)	0.6157 (2)	4.3 (1)
C(24)	0.3764 (7)	0.4727 (5)	0.6673 (2)	3.8 (1)
C(25)	0.2213 (8)	0.5058 (6)	0.5296 (2)	4.6 (2)
C(100)	0.0545 (10)	0.7118 (9)	-0.0193 (4)	8.1 (3)
C(101)	0.0090 (11)	0.7472 (8)	-0.0689 (3)	6.9 (2)

Table 2. Selected bond distances (\AA) and angles ($^\circ$) in $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4(4\text{-CN-py})_2 \cdot \text{CH}_3\text{CN}$

Bond distances and angles not shown have been deposited (see deposition footnote).

Rh(1)–Rh(2)	2.393 (1)	O(2)–C(1)	1.263 (6)
–O(1)	2.051 (3)	O(3)–C(3)	1.263 (6)
–O(3)	2.045 (3)	O(4)–C(3)	1.270 (6)
O(5)	2.050 (3)	O(5)–C(5)	1.270 (6)
–O(7)	2.025 (3)	O(6)–C(5)	1.253 (6)
N(1)	2.244 (4)	O(7)–C(7)	1.270 (6)
Rh(2)–O(2)	2.031 (3)	O(8)–C(7)	1.255 (6)
O(4)	2.045 (3)	C(1)–C(2)	1.505 (7)
O(6)	2.041 (3)	C(3)–C(4)	1.513 (7)
–O(8)	2.032 (3)	C(5)–C(6)	1.532 (7)
N(2)	2.243 (4)	C(7)–C(8)	1.508 (7)
O(1)–C(1)	1.269 (6)		
Rh(2)–Rh(1)–O(1)	87.8 (1)	O(2)–Rh(2)–O(6)	176.4 (1)
–O(3)	88.5 (1)	O(8)	88.1 (1)
O(5)	87.3 (1)	–N(2)	89.3 (1)
O(7)	87.73 (9)	O(4)–Rh(2)–O(6)	90.0 (2)
–N(1)	176.8 (1)	O(8)	175.6 (1)
O(1)–Rh(1)–O(3)	88.9 (1)	N(2)	93.0 (1)
–O(5)	175.1 (1)	O(6)–Rh(2)–O(8)	90.8 (1)
O(7)	90.5 (1)	N(2)	94.1 (1)
N(1)	89.8 (1)	O(8)–Rh(2)–N(2)	91.3 (1)
O(3)–Rh(1)–O(5)	90.7 (1)	O(1)–C(1)–O(2)	124.2 (4)
O(7)	176.2 (1)	C(2)	118.3 (4)
N(1)	93.4 (1)	O(2)–C(1)–C(2)	117.5 (5)
O(1)–Rh(1)–O(7)	89.5 (1)	O(3)–C(3)–O(4)	125.9 (5)
N(1)	95.1 (1)	C(4)	117.0 (5)
O(7)–Rh(1)–N(1)	90.3 (1)	O(4)–C(3)–C(4)	117.0 (5)
Rh(1)–Rh(2)–O(2)	87.8 (1)	O(5)–C(5)–O(6)	126.5 (5)
–O(4)	87.6 (1)	C(6)	116.5 (5)
O(6)	88.7 (1)	O(6)–C(5)–C(6)	117.0 (5)
–O(8)	88.0 (1)	O(7)–C(7)–O(8)	125.5 (5)
N(2)	177.1 (1)	C(8)	116.6 (5)
O(2)–Rh(2)–O(4)	90.9 (1)	O(8)–C(7)–C(8)	118.0 (5)

Discussion. Table 1 records the final positional and equivalent isotropic thermal parameters for the 37 nonhydrogen atoms in the structure. Table 2 presents some selected bond distances and angles.* Fig. 1 gives a view of the dirhodium adduct with the atom labeling scheme shown. The atoms of the acetonitrile molecule include N(100), C(100), and C(101). A stereoscopic diagram of the unit-cell contents of Rh₂(O₂CCH₃)₄(4-CN-py)₂.CH₃CN is depicted in Fig. 2.

The structure consists of molecules of Rh₂(O₂CCH₃)₄(4-CN-py)₂ and CH₃CN that reside on general positions in the unit cell. Although there is no crystallographically imposed symmetry in the dirhodium molecule, the Rh₂(O₂CC)₄ core approximates *D*_{4h} symmetry as found in other metal-metal bonded tetrakis(carboxylato)dimetal(II) complexes (Cotton & Walton, 1982). The Rh(1)–Rh(2) bond length is 2.393 (1) Å with the axial pyridine N atoms N(1) and N(2) coordinated to Rh(1) and Rh(2), respectively, at distances of 2.244 (4) and 2.243 (4) Å. The axial Rh–Rh–N angles are close to linear with values of 176.8 (1) and 177.1 (1)°. The Rh atoms are displaced out of the equatorial acetate oxygen planes towards the axial 4-CN-py nitrogen atoms by 0.069 and 0.077 Å for Rh(1) and Rh(2), respectively.

The present structure is very closely similar to the structure of Rh₂(O₂CCH₃)₄(py)₂ (Koh & Christoph, 1978). The stronger py ligand gives rise to an axial Rh–N distance that is 0.016 Å shorter than the corresponding 4-CN-py structure with a concomitant increase in the Rh–Rh distance by 0.0033 Å. For these two ligands the bonding trends closely follow that expected from purely Rh–N σ-bonding effects in agreement with SCF-Xα-SW calculations (Norman & Kolari, 1978) for weak σ-donor ligands having the energies of the lone-pair orbitals far removed from the Rh–Rh π manifold. Photoelectron data (Dennis, Howard, Kadish, Bear, Brace & Winograd, 1980) for the monoadduct Rh₂(O₂CCH₃)₄(4-CN-py) support this contention with a decrease in the Rh 3*d*_{5/2} and O 1s binding energies relative to the anhydrous Rh₂(O₂CCH₃)₄ dimer. Extensive π interactions would result in an increase in the electron density on the Rh₂(O₂CCH₃)₄ unit with an increase in the binding energies for these atoms. A comparison of some average dimensions in the Rh₂(O₂CCH₃)₄ frameworks shows that the py and 4-CN-py diadducts are practically identical: Rh–O 2.039 (2), 2.040 (3) Å; C–O 1.266 (3), 1.264 (3) Å; Rh–Rh–O 87.98 (6), 87.9 (1)°; Rh–O–C 119.1 (1), 119.3 (3)°; and O–

C–O 125.7 (1), 125.5 (5)°. No pair of dimensions shows a difference of more than one standard deviation.

Although the Rh₂(O₂CR)₄ framework in general is quite unresponsive to changes occurring in the Rh–Rh and Rh–N bond lengths, it should be noted that the py and 4-CN-py adducts represent only about 5% of the total range of Rh–Rh bond lengths with axial nitrogen donor ligands. The range is currently bounded by Rh₂(O₂CCH₃)₄(CH₃CN)₂ (Cotton & Thompson, 1981) and Rh₂(O₂CCH₃)₄(NO)(NO₂) (Koh, 1979) with Rh–Rh bond lengths of 2.384 (1) and 2.4537 (4) Å, respectively. Thus, while most adducts that have been structurally characterized including the 4-CN-py adduct here show long Rh–N axial bonds that can be accommodated by the calculations of Norman & Kolari in terms of bonding interactions, it is clear that the extremely short axial distances in the mixed NO–NO₂ adduct [Rh–N = 1.927 (4), 2.008 (4) Å] will require an explanation analogous to that developed for phosphine adducts of tetrakis(carboxylato)dirhodium(II) (Bursten & Cotton, 1981).

Inspection of the bonding about the 4-CN-py molecules reveals that the orientation with respect to the Rh₂(O₂CCH₃)₄ unit is controlled by intermolecular contacts (*cf.* Fig. 2). The two 4-CN-py molecules are inclined at an angle of 31.1° to one another. For the py diadduct (Koh & Christoph, 1978) this angle increases to 59°; both diadducts fall short of the 90° orientation of pyridine rings expected for a strong Rh–N π interaction consistent with the weak σ bonding in these molecules discussed above. The pyridine rings in the 4-CN-py diadduct are planar with no deviations greater than 0.010 Å. A distinct bending of the 4-CN-py molecules away from perpendicularity to the RhO₄ planes is evident in both Figs. 1 and 2. This distortion due to interactions with the *p*-cyano groups cannot be discerned by inspection of the Rh–Rh–N angles that are close to linearity, but examination of the Rh–N...C angles, namely Rh(1)–N(1)...C(12) and Rh(2)–N(2)...C(22), shows values of 172.9 (4) and 168.9 (4)°.

Comparison of average bond distances and angles within the 4-CN-py molecule in Rh₂(O₂CCH₃)₄(4-CN-py)₂ with those in the free ligand (Laing, Sparrow & Sommerville, 1971) reveals very small deviations as seen from the following values: C–N_{ring} 1.342 (7), 1.331 (6) Å; C–C_{ring} 1.385 (8), 1.382 (6) Å; C–C_{cyano} 1.447 (8), 1.439 (8) Å; C–N_{cyano} 1.133 (8), 1.137 (8) Å; C–N–C 118.7 (5), 117.8 (3)°; N–C–C 122.8 (8), 122.7 (3)°; and C–C–C 118.6 (6), 118.9 (3)°. These data suggest again that Rh–N bonding is purely of the σ-type, for much greater changes in the pyridine ring dimensions are expected if π interactions are present. A similar argument was advanced (Steffen & Palenik, 1977) based on structural data to characterize the bonding in various tetrahedral zinc complexes including Zn(4-CN-py)₂Cl₂.

* Lists of non-essential bond distances and angles, anisotropic thermal parameters, least-squares planes, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38814 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of a Novel One-Dimensional Chlorpromazine–Copper(II) Complex Salt, $*[\text{C}_{17}\text{H}_{20}\text{ClN}_2\text{S}]_2[\text{CuCl}_4]_2$

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Abstract. $M_r = 1050.4$, orthorhombic, $Pnma$, $a = 23.745(4)$, $b = 13.897(3)$, $c = 12.580(2)$ Å, $V = 4151.2$ Å³, $Z = 4$, $D_x = 1.684$, D_m (flotation in CCl_4/EtOH) = 1.622 Mg m⁻³, $\mu(\text{Mo } K\alpha: \lambda = 0.71069$ Å) = 1.70 mm⁻¹, $F(000) = 2128$, room temperature. The structure was solved by the heavy-atom method and refined to a final R value of 0.057 for 2161 observed reflections. In the crystal, to equilibrate the charge of the CuCl_4^{2-} , each chlorpromazine moiety needs a charge of 2+. Protonation of the N atom in the side chain accounts for 1+, and the other positive charge is spread over the phenothiazine ring resulting in the formation of a dimeric pair of chlorpromazines. In the pair of phenothiazine rings, the S–S' distance of 2.944(3) Å is extremely short suggesting some bonding interaction. The dimeric pairs stack one-dimensionally along b .

* 2-Chloro-10-(3-dimethylammoniopropyl)phenothiazinium tetrachlorocuprate(II).

Introduction. The structure of complexes formed through interactions between neuroleptics and copper ions is an interesting subject in connection with various important functions of copper enzymes in the human brain. However, reports on detailed X-ray structural analyses of the resultant complexes seem to be limited to those of diazepam as the anti-anxiety drug (Mosset, Tuchagues, Bonnet, Haran & Sharrock, 1980; Miyamae, Obata & Kawazura, 1982).

Chlorpromazine hydrochloride [2-chloro-10-(3-dimethylaminopropyl)phenothiazine hydrochloride, CPZ.HCl], one of the major tranquilizers well known on account of its outstanding effect, yields a black crystalline complex of composition $[\text{C}_{17}\text{H}_{20}\text{ClN}_2\text{S}][\text{CuCl}_4]$ when treated with CuCl_2 in ethanol containing HCl.

X-ray diffraction analysis of this crystal has revealed that in the complex, a pair of CPZ.H moieties piles up one-dimensionally as though necessitated by the CuCl_4^{2-} anions.