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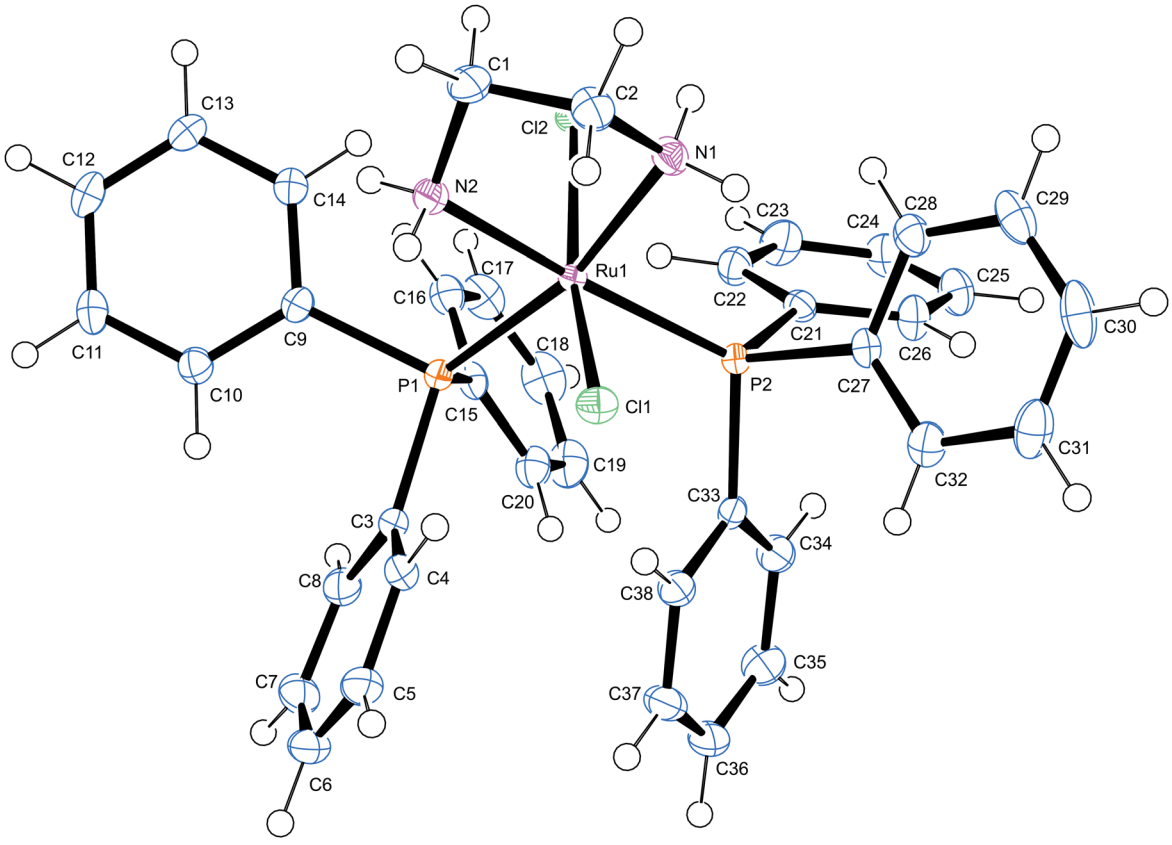
The crystal structure of *trans*-dichlorido-(ethylenediamine-κ^2N,N')-bis(triphenylphosphine-κ^1P)ruthenium(II), $C_{38}H_{38}Cl_2N_2P_2Ru$



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Abstract

$C_{38}H_{38}Cl_2N_2P_2Ru$, monoclinic, $P2_1/c$ (no. 14), a = 10.8827(3) Å, b = 30.6226(7) Å, c = 20.2089(4) Å, β = 93.8560(10)°, V = 6719.5(3) Å^3, Z = 8, $R_{gt}(F)$ = 0.0306, $wR_{ref}(F^2)$ = 0.0636, T = 173(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Source of materials

All reagents are commercially available and were used without further purification. The reaction was carried

Table 1: Data collection and handling.

Crystal:	Yellow plate
Size:	0.52 × 0.37 × 0.02 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.75 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Photon, ω
θ_{max}, completeness:	28.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	139,125, 16,216, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs}°>°2σ(I_{obs}), 14,939
N(param)$_{refined}$:	843
Programs:	Bruker [1], Shelx [2], WinGX [3], Platon [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.0124 (2)	0.28312 (7)	0.54311 (11)	0.0244 (4)
H1A	0.0205	0.313013	0.538305	0.029*
H1B	−0.09667	0.285259	0.558493	0.029*
C2	−0.0144 (2)	0.25925 (7)	0.47801 (11)	0.0239 (4)
H2A	−0.073009	0.273449	0.445143	0.029*
H2B	0.068474	0.259721	0.46059	0.029*
C3	0.28840 (18)	0.16301 (6)	0.70461 (10)	0.0176 (4)
C4	0.37167 (19)	0.17315 (7)	0.65730 (10)	0.0205 (4)
H4	0.342785	0.18632	0.616629	0.025*
C5	0.4963 (2)	0.16418 (7)	0.66907 (12)	0.0274 (5)
H5	0.551315	0.169652	0.635487	0.033*
C6	0.5405 (2)	0.14731 (7)	0.72952 (13)	0.0309 (5)
H6	0.626005	0.141807	0.737854	0.037*
C7	0.4598 (2)	0.13846 (7)	0.77779 (12)	0.0294 (5)
H7	0.490275	0.127606	0.819771	0.035*
C8	0.3343 (2)	0.14539 (7)	0.76512 (11)	0.0229 (4)
H8	0.2791	0.138089	0.79789	0.027*
C9	0.11743 (18)	0.22668 (6)	0.74343 (10)	0.0173 (4)
C10	0.21399 (19)	0.23821 (7)	0.78965 (10)	0.0193 (4)
H10	0.28799	0.221665	0.791674	0.023*
C11	0.2037 (2)	0.27331 (7)	0.83252 (10)	0.0227 (4)
H11	0.269648	0.280163	0.864006	0.027*
C12	0.0970 (2)	0.29838 (7)	0.82938 (10)	0.0238 (4)
H12	0.090095	0.322572	0.858327	0.029*
C13	0.0011 (2)	0.28789 (7)	0.78387 (11)	0.0242 (4)
H13	−0.071861	0.305005	0.781421	0.029*
C14	0.0110 (2)	0.25229 (7)	0.74151 (11)	0.0220 (4)
H14	−0.056023	0.245306	0.710746	0.026*
C15	0.04788 (19)	0.13770 (7)	0.73980 (9)	0.0183 (4)
C16	−0.0537 (2)	0.14923 (7)	0.77506 (10)	0.0234 (4)
H16	−0.077866	0.178977	0.777181	0.028*
C17	−0.1196 (2)	0.11756 (8)	0.80701 (11)	0.0290 (5)
H17	−0.187981	0.125803	0.83104	0.035*
C18	−0.0859 (2)	0.07421 (8)	0.80393 (12)	0.0338 (5)
H18	−0.132754	0.052561	0.824622	0.041*
C19	0.0163 (2)	0.06222 (8)	0.77063 (11)	0.0303 (5)
H19	0.040571	0.032457	0.769361	0.036*
C20	0.0831 (2)	0.09385 (7)	0.73910 (10)	0.0233 (4)
H20	0.153504	0.085517	0.716793	0.028*
C21	−0.13460 (18)	0.08326 (6)	0.57535 (10)	0.0167 (4)
C22	−0.18810 (19)	0.08935 (7)	0.63535 (10)	0.0221 (4)
H22	−0.1612	0.112686	0.663716	0.026*
C23	−0.2808 (2)	0.06147 (8)	0.65411 (12)	0.0293 (5)
H23	−0.315885	0.065741	0.695406	0.035*
C24	−0.3220 (2)	0.02765 (8)	0.61312 (12)	0.0301 (5)
H24	−0.384723	0.008604	0.626386	0.036*
C25	−0.2717 (2)	0.02160 (8)	0.55265 (12)	0.0282 (5)
H25	−0.300689	−0.001283	0.523949	0.034*
C26	−0.1787 (2)	0.04910 (7)	0.53421 (11)	0.0234 (4)
H26	−0.144229	0.044689	0.492782	0.028*
C27	−0.01424 (18)	0.10713 (6)	0.46422 (9)	0.0165 (4)
C28	−0.1190 (2)	0.12468 (7)	0.43008 (10)	0.0213 (4)
H28	−0.177133	0.140392	0.453836	0.026*
C29	−0.1391 (2)	0.11948 (7)	0.36237 (11)	0.0270 (5)
H29	−0.21	0.132068	0.339908	0.032*
C30	−0.0569 (2)	0.09611 (8)	0.32703 (11)	0.0306 (5)
H30	−0.071241	0.092527	0.280454	0.037*
C31	0.0463 (2)	0.07796 (8)	0.35993 (11)	0.0295 (5)
H31	0.102612	0.061585	0.335914	0.035*
C32	0.0682 (2)	0.08358 (7)	0.42829 (10)	0.0224 (4)
H32	0.139735	0.071248	0.450434	0.027*
C33	0.12525 (18)	0.07575 (6)	0.58006 (9)	0.0163 (4)
C34	0.1019 (2)	0.03399 (7)	0.60410 (11)	0.0222 (4)
H34	0.019418	0.023941	0.604977	0.027*
C35	0.1987 (2)	0.00706 (7)	0.62674 (12)	0.0276 (5)
H35	0.181956	−0.021219	0.643255	0.033*
C36	0.3190 (2)	0.02118 (7)	0.62536 (12)	0.0277 (5)
H36	0.384725	0.002853	0.641523	0.033*
C37	0.3435 (2)	0.06210 (7)	0.60036 (12)	0.0268 (5)
H37	0.426242	0.071594	0.598376	0.032*
C38	0.24738 (19)	0.08926 (7)	0.57820 (10)	0.0205 (4)
H38	0.264951	0.117424	0.561532	0.025*
N1	−0.05294 (17)	0.21356 (6)	0.48960 (9)	0.0194 (3)
N2	0.06769 (17)	0.25783 (6)	0.59095 (9)	0.0194 (3)
P1	0.12456 (5)	0.17786 (2)	0.68852 (2)	0.01457 (9)
P2	0.00209 (4)	0.11506 (2)	0.55466 (2)	0.01381 (9)
Cl1	0.21032 (4)	0.19031 (2)	0.51273 (2)	0.01898 (9)
Cl2	−0.16861 (4)	0.19859 (2)	0.62038 (2)	0.02013 (10)
Ru1	0.03478 (2)	0.18852 (2)	0.58171 (2)	0.01280 (4)
H1C	−0.037 (2)	0.1977 (8)	0.4553 (13)	0.020 (6)*
H1D	−0.131 (2)	0.2126 (8)	0.4940 (11)	0.017 (6)*
H2C	0.059 (3)	0.2680 (9)	0.6300 (14)	0.034 (7)*
H2D	0.143 (2)	0.2620 (8)	0.5829 (12)	0.022 (6)*
C39	0.5441 (2)	0.26225 (7)	0.76100 (11)	0.0234 (4)
H39A	0.474037	0.244633	0.742064	0.028*
H39B	0.564483	0.252535	0.807166	0.028*
C40	0.6535 (2)	0.25684 (7)	0.72036 (11)	0.0237 (4)
H40A	0.724101	0.274013	0.739768	0.028*
H40B	0.678044	0.225744	0.718941	0.028*
C41	0.55621 (19)	0.29347 (7)	0.50086 (10)	0.0208 (4)
C42	0.4902 (2)	0.25525 (7)	0.51131 (11)	0.0245 (4)
H42	0.42575	0.255726	0.540746	0.029*
C43	0.5173 (2)	0.21640 (8)	0.47931 (12)	0.0292 (5)
H43	0.471133	0.190796	0.487141	0.035*
C44	0.6101 (2)	0.21489 (8)	0.43658 (11)	0.0284 (5)
H44	0.629491	0.188281	0.415472	0.034*

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C45	0.6750 (2)	0.25257 (9)	0.42465 (11)	0.0305 (5)
H45	0.738261	0.251859	0.39447	0.037*
C46	0.6488 (2)	0.29175 (8)	0.45646 (11)	0.0263 (5)
H46	0.694426	0.317337	0.44776	0.032*
C47	0.36822 (19)	0.35909 (7)	0.50314 (10)	0.0198 (4)
C48	0.3038 (2)	0.33294 (8)	0.45615 (11)	0.0260 (5)
H48	0.336792	0.305483	0.444538	0.031*
C49	0.1919 (2)	0.34664 (9)	0.42619 (11)	0.0304 (5)
H49	0.147982	0.328182	0.395082	0.036*
C50	0.1439 (2)	0.38689 (9)	0.44126 (12)	0.0339 (6)
H50	0.068028	0.39633	0.419991	0.041*
C51	0.2068 (2)	0.41344 (9)	0.48745 (12)	0.0339 (6)
H51	0.174312	0.441206	0.497916	0.041*
C52	0.3180 (2)	0.39933 (8)	0.51860 (11)	0.0260 (5)
H52	0.360112	0.417446	0.550847	0.031*
C53	0.62280 (19)	0.38282 (7)	0.50932 (10)	0.0206 (4)
C54	0.5857 (2)	0.41411 (8)	0.46256 (11)	0.0297 (5)
H54	0.502098	0.415205	0.445824	0.036*
C55	0.6697 (3)	0.44389 (10)	0.43991 (14)	0.0448 (7)
H55	0.642787	0.465701	0.408788	0.054*
C56	0.7921 (3)	0.44186 (11)	0.46252 (13)	0.0455 (7)
H56	0.849141	0.462496	0.447493	0.055*
C57	0.8314 (2)	0.40984 (10)	0.50694 (12)	0.0364 (6)
H57	0.916262	0.407628	0.520932	0.044*
C58	0.7475 (2)	0.38076 (8)	0.53135 (11)	0.0265 (5)
H58	0.77483	0.359405	0.563115	0.032*
C59	0.49722 (18)	0.45120 (6)	0.67967 (10)	0.0179 (4)
C60	0.5850 (2)	0.45537 (7)	0.63336 (11)	0.0238 (4)
H60	0.603358	0.431056	0.606538	0.029*
C61	0.6466 (2)	0.49475 (8)	0.62567 (13)	0.0326 (5)
H61	0.70574	0.497234	0.593384	0.039*
C62	0.6218 (2)	0.53007 (8)	0.66480 (13)	0.0321 (5)
H62	0.664659	0.556801	0.660061	0.038*
C63	0.5337 (2)	0.52641 (7)	0.71134 (12)	0.0296 (5)
H63	0.51605	0.550737	0.738284	0.035*
C64	0.4720 (2)	0.48761 (7)	0.71839 (10)	0.0233 (4)
H64	0.411504	0.485513	0.749997	0.028*
C65	0.43584 (18)	0.39910 (6)	0.78562 (9)	0.0168 (4)
C66	0.54700 (19)	0.41198 (7)	0.81881 (10)	0.0199 (4)
H66	0.613594	0.421026	0.793986	0.024*
C67	0.5610 (2)	0.41166 (7)	0.88779 (11)	0.0248 (4)
H67	0.636071	0.421391	0.909674	0.03*
C68	0.4665 (2)	0.39730 (8)	0.92459 (11)	0.0276 (5)
H68	0.476442	0.397127	0.971659	0.033*
C69	0.3575 (2)	0.38318 (8)	0.89262 (11)	0.0269 (5)
H69	0.293231	0.372432	0.917711	0.032*
C70	0.3416 (2)	0.38467 (7)	0.82352 (10)	0.0217 (4)
H70	0.265423	0.375715	0.802057	0.026*
C71	0.25885 (18)	0.40915 (7)	0.67548 (10)	0.0181 (4)
C72	0.2120 (2)	0.44993 (7)	0.65632 (11)	0.0245 (4)
H72	0.266866	0.47359	0.650842	0.029*
C73	0.0856 (2)	0.45637 (8)	0.64513 (12)	0.0285 (5)
H73	0.05514	0.484353	0.631994	0.034*
C74	0.0042 (2)	0.42253 (8)	0.65292 (11)	0.0269 (5)
H74	−0.081954	0.427227	0.646026	0.032*
C75	0.0492 (2)	0.38177 (8)	0.67082 (11)	0.0250 (4)

Table 2: (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H75	−0.006281	0.358185	0.675407	0.03*
C76	0.17499 (19)	0.37502 (7)	0.68217 (11)	0.0224 (4)
H76	0.204617	0.346821	0.694653	0.027*
N3	0.51191 (19)	0.30924 (6)	0.75966 (9)	0.0208 (4)
N4	0.61608 (18)	0.27282 (6)	0.65257 (9)	0.0207 (4)
P3	0.51692 (5)	0.34401 (2)	0.54589 (2)	0.01628 (10)
P4	0.42488 (4)	0.39787 (2)	0.69344 (2)	0.01463 (9)
Cl3	0.33416 (4)	0.29107 (2)	0.64009 (2)	0.02071 (10)
Cl4	0.71837 (4)	0.36305 (2)	0.69438 (2)	0.02141 (10)
Ru2	0.51755 (2)	0.33391 (2)	0.65935 (2)	0.01352 (4)
H3A	0.569 (3)	0.3237 (9)	0.7840 (14)	0.036 (8)*
H3B	0.440 (3)	0.3125 (9)	0.7733 (13)	0.028 (7)*
H4A	0.566 (3)	0.2530 (10)	0.6326 (14)	0.039 (8)*
H4B	0.682 (3)	0.2743 (8)	0.6295 (13)	0.028 (7)*

out under an argon atmosphere using standard Schlenk techniques. The title compound was synthesized by dissolving dichloridotris(triphenylphosphine) ruthenium(III) (0.500 g, 0.522 mmol) in CH_2Cl_2 (10 mL). To this solution was added, drop-wise, ethylenediamine (0.039 mL, 0.58 mmol) dissolved in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h. The resulting brownish solution was filtered to remove any insoluble impurities, and the solution was concentrated under reduced pressure. The product was then precipitated by adding *n*-hexane. The yellow solid obtained was filtered and washed with diethyl ether (3 × 10 mL), to give the product in 85% yield. Yellow plate crystals suitable for X-ray diffraction analysis were obtained after five days by slow diffusion of hexane into a dichloromethane solution of the complex.

Experimental details

Intensity data was determined on a Bruker Venture D8 Photon CMOS diffractometer with graphite-monochromated $MoK_{\alpha1}$ (λ = 0.71073 Å) radiation at 173 K using an Oxford Cryostream 600 cooler. Data reduction was carried out using the program Saint+, version 6.02 [1] and empirical absorption corrections were made using Sadabs [1]. Space group assignments was made using Xprep [1]. The structure was solved in the WinGX [2] Suite of programs, using intrinsic phasing through Shelxt [3] and refined using full-matrix least-squares/difference Fourier techniques on F^2 using Shelxl-2017 [3]. All C bound hydrogen atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times those of their parent atoms. N-bound hydrogen atoms were located in

the difference Fourier map and their coordinates and isotropic displacement parameters refined freely. Diagrams and publication material were generated using Ortep-3 [3], and Platon [4].

Comment

Ethylenediamine is the most widely studied bidentate nitrogen donor ligand in coordination chemistry [5]. The ethylenediamine molecule can adopt either a *cis* or *trans* conformation, due to rotation about the C–C bond [5, 6]. However, once it is coordinated to a metal atom in a bidentate chelating mode, the *cis* conformation of the ligand is enforced.

The chemistry of ruthenium(II) complexes have been extensively studied due to their versatility and wide range of applications in several fields; such as bioinorganic chemistry, catalysis, supramolecular and photochemistry [7]. Ruthenium complexes with chlorido and dimethylsulfoxide (DMSO) ligands have been shown to have potential application as chemotherapeutic agents [8]. Also, Ru(II) complexes with chelating diamine or diphosphine ligands have gained much attention due to their applications in catalysis and potential antimicrobial activity [7–10].

Biologically, chelation is important because it has been shown that coordinating a metal ion to a ligand in this manner, has the potential of reducing the polarity of the metal ion as there will be partial sharing of the positive charge of the metal with the donor atoms of the ligand [11]. This property enhances the lipophilicity of the complex, thus increasing its permeation through the lipid membrane of the bacterial cell. It has also been reported that coordinating a ligand to a metal ion synergistically enhances the biological activity of the ligand while minimizing the cytotoxic effect of metal ion and ligand [7].

The title compound crystallizes in the monoclinic space group $P2_1/c$ (no. 14), with its unit cell filled with two complexes. The bond lengths and angles are within the normal ranges and are comparable to related structures [7, 12, 13]. The ruthenium atom is coordinated in a distorted octahedral geometry with an ethylenediamine ligand chelated via the two nitrogen (N1 and N2) atoms, two monodentate P-donor triphenylphosphine (PPh_3) ligands and two chlorides in a mutually trans position. The two chloride anions are bent away from their axial positions, toward the diamine ligand due to the steric effect of the bulky PPh_3 ligands [7]. The distortion from linearity for the axial ligands Cl2–Ru1–Cl1 was measured at 162.06°. Similarly, the bulkiness of the phenyl groups of PPh_3 resulted in the distortion of the P1–Ru1–P2 angle to 97.45°.

Bazargan et al. [5], conducted a full structural and geometrical study using the Cambridge Structural Database (CSD) combined with theoretical calculations, for various five-membered N-donor chelate rings and their complexes of various transition and non-transition metals. One of the findings of the study showed that for the ethylenediamine ligand bonded to a 4*d* metal ion, the ideal average N–M bond length is 2.115 Å and the N–M–N angle is 81.2°. These results are supported by the findings obtained in the current study, with the average N–M distance of 2.166 Å and N–M–N angle of 77.76°. The observed small difference in bond length and angles is in agreement with the previously observed trend between M–N bond length and the chelate bite angle which is inversely proportional [5]. In addition, there are two strong intermolecular hydrogen bonds between the amine group of one complex and the chloride atom of a second complex, with the distance of H2D···Cl3 at 2.48°Å and H4B···Cl2 at 2.85 Å.

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