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Crystal Structure of Bis(1,5-dithiacyclooctane)nickel(II) Chloride[1]

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Bis(1,5-dithiacyclooctane)nickel(II) chloride, $Ni(C_6H_{12}S_2)_2Cl_2$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 9.459$ (3) Å, $b = 11.704$ (4) Å, $c = 7.925$ (3) Å, and $\beta = 99.20$ (1)°. There are two formula units per unit cell. The crystal structure was determined by Patterson and Fourier techniques and was refined by least-squares calculations, using 1707 Mo Kα reflections measured on a Picker automatic diffractometer. The final R index is 0.046. The arrangement at the nickel atom is a distorted octahedron with the sulfur atoms defining an equatorial plane and chlorine atoms in the axial positions. The Ni–Cl distance is 2.358 (3) Å and the Ni–S distances are 2.478 (3) and 2.497 (3) Å. The ligand molecules bridge the nickel atoms, forming a two-dimensional network. There is disorder in the ligand molecule; it adopts both chair-boat and double-chair (crown) conformations.

Bis(1,5-dithiacyclooctane)nickel(II) chloride was prepared as part of a continuing study of transition metal complexes of medium-ring ligands containing two donor atoms.[2-5] The dithioether ligand in this complex is analogous to the diamine 1,5-diazacyclooctane (daco) from which only square-planar bis complexes of nickel(II) and copper(II) have been prepared with perchlorate and chloride as anions. In these complexes daco was assumed to be chelated as observed for the analogous seven-membered ring 1,4-diazacycloheptane (dach) in the complex $[Cu(dach)_2NO_3]NO_3 \cdot [Cu(dach)_2H_2O](NO_3)_2$.[3] Molecular models indicate that in bis-chelated daco complexes the structure achieving the least strain has the donor atoms defining an equatorial plane, with the ligands adopting boat-chair conformations with the boat portions of the two ligands trans to each other[2] (Figure 1). The axial positions of the metal atom are effectively blocked under these conditions. Any twisting or change in conformation of the ligand which opens the axial positions increases intra- and interligand interactions within the complex, thus explaining the lack of any octahedral $(daco)_2$ complex. The boat-chair conformation of the daco moiety and its effectiveness in blocking one axial position were demonstrated in the crystal structure determination of 1,5-diazacyclooctane-*N,N'*-diacetatoaquonickel(II) dihydrate.[6] A crystal structure of a five-coordinate $(daco)_2$ complex, $[Co(daco)_2Cl]Cl$, has recently been completed.[7] The coordination geometry is square pyramidal with the daco ligands coordinated at the equatorial positions. Methylene carbons on both ligands are bent back from one axial position allowing coordination by chlorine; the three remaining carbons at the other end of each ligand describe an approximate plane with the two nitrogens and lie close to the other axial position blocking further coordination. In all known cases chelation of a 1,5-diheterocyclooctane ligand causes blockage of one axial position.

Chelation of the dithioether ligand 1,5-dithiacyclooctane (dtco) has been indicated by the observation of 1:1 tetrahedral nickel(II) bromide and iodide species in solution,[5] as well as by the square-planar $(dtco)_2Ni^{II}$ complexes prepared with perchlorate and tetrafluoroborate as anions.

Therefore, the observation of an octahedral spectrum for the solid complex bis(1,5-dithiacyclooctane)nickel(II) chloride[5] was unexpected. In order to expose both axial positions to additional coordination the dtco ligands cannot be chelated to the nickel atom. Two structures which avoid chelation are a linear polymer of nickel atoms connected by two bridging ligands and a planar array of nickel atoms interconnected by bridging ligands.

In order to distinguish between these possibilities this crystal structure determination was undertaken. Many octahedral nickel(II) complexes containing thioether donors have been prepared,[8-14] but no crystal structure determination has been reported.

Experimental Section

Bis(1,5-dithiacyclooctane)nickel(II) chloride[5] was prepared by adding 2.5 ml of 1,5-dithiacyclooctane to a concentrated ethanolic solution of anhydrous nickel(II) chloride (1.0 g in 10 ml) and allowing the resulting mixture to stand until all of the initially precipitated brown solid had changed to yellow-green crystals. The crystals were washed with absolute ethanol and anhydrous ether and were dried *in vacuo*. The crystals decompose under prolonged exposure to air.

The space group was determined from Weissenberg and precession photographs taken with Cu Kα radiation; the crystals used were coated with glue. The systematic extinctions ($h0l$ absent for $(h + l)$ odd, $0k0$ absent for k odd) determined the space group to be $P2_1/n$ ($C_{2h}{}^5$).

For gathering three-dimensional intensity data a large, clear crystal was ground to a sphere of 0.35-mm diameter; a small portion of the sphere was cleaved off. The crystal was coated with Eastman 910 adhesive to prevent decomposition and was mounted on a Picker automatic diffractometer equipped with a full-circle goniostat. Monochromatic Mo Kα radiation (graphite crystal) was used. The crystal orientation was determined and the cell parameters were calculated from 18 2θ, χ, ϕ sets measured manually.

The resulting cell dimensions are $a = 9.459$ (3) Å, $b = 11.704$ (4) Å, $c = 7.925$ (3) Å, $\beta = 99.20$ (1)°, and $V = 866.1$ Å^3 at 23–24° using λ(Mo Kα_1) 0.70926 Å. The density calculated from a formula weight of 426.20 (for $Ni(C_6H_{12}S_2)_2Cl_2$), $Z = 2$, and the parameters given above (1.63 g cm^{-3}) agrees well with the density measured using the flotation method (1.64 g cm^{-3}).

A total of 1866 unique reflections were scanned by the θ–2θ method at a 2θ scan speed of 1° min^{-1}. Stationary background counts of 20-sec duration were taken at each end of the scan range, but because of a small error (0.07°) in the ω origin assignment for the

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Table I. Final Fractional Coordinates and Anisotropic Temperature Factors (Å^2)[a,b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	2.38 (8)	1.72 (7)	1.97 (7)	−0.11 (5)	−0.01 (5)	0.10 (5)
Cl	−0.1257 (3)	0.0446 (2)	0.2254 (3)	3.48 (10)	3.20 (10)	2.59 (9)	0.30 (7)	−0.65 (7)	−0.40 (7)
S(1)	0.2002 (2)	0.1109 (2)	0.1617 (2)	2.19 (8)	2.21 (8)	2.35 (8)	−0.28 (6)	0.13 (6)	−0.12 (6)
S(2)	0.4025 (3)	0.3186 (2)	0.3621 (3)	3.03 (9)	1.80 (8)	2.53 (9)	−0.07 (5)	−0.01 (7)	−0.28 (6)
C(1)	0.2404 (15)	0.0509 (11)	0.3740 (15)	4.7 (6)	2.8 (4)	2.8 (4)	−1.5 (4)	−0.8 (4)	0.5 (4)
C(2)	0.3490 (30)	0.1032 (20)	0.4988 (26)	12.4 (14)	9.5 (9)	3.6 (8)	−8.1 (8)	−2.8 (8)	2.8 (7)
C(3)	0.4134 (29)	0.2093 (14)	0.5255 (23)	11.6 (15)	3.6 (7)	4.4 (8)	−3.4 (8)	−4.0 (9)	1.5 (6)
C(4)	0.5181 (15)	0.2623 (15)	0.2217 (25)	3.9 (5)	5.4 (8)	9.1 (11)	−1.8 (5)	3.0 (6)	−4.7 (8)
C(5)	0.4489 (19)	0.2006 (16)	0.0639 (25)	6.0 (8)	6.4 (8)	7.2 (10)	−3.5 (7)	4.3 (8)	−3.9 (8)
C(6)	0.3655 (13)	0.0925 (12)	0.0783 (18)	3.4 (5)	4.3 (5)	4.8 (6)	−0.9 (4)	1.3 (4)	−1.7 (4)

[a] Numbers in parentheses are estimated standard deviations in the last digit. [b] B_{ij} are coefficients in the temperature factor expression $\exp[-{}^1/_4(a^{*2}B_{11}h^2 + b^{*2}B_{22}k^2 + c^{*2}B_{33}l^2 + 2a^*b^*B_{12}hk + 2a^*c^*B_{13}hl + 2b^*c^*B_{23}kl)]$.

setting program, the scan range was not quite symmetrical (the intended scan range for all reflections was $[2\theta(\alpha_1) - 1.00°]$ to $[2\theta(\alpha_2) + 1.00°]$), and we decided to use only the high-angle background count in estimating the total background. Niobium foil attenuation filters were used to reduce coincidence losses. The intensities of 18 reflections were measured periodically to check electronic and crystal stability (IUCr radiation damage survey[15]). No systematic drift was observed. A total of 1707 reflections exceeded 3 times the estimated standard deviation (counting statistics) and were used in the structure calculations. The intensities were corrected for Lorentz and monochromator polarization factors and for absorption (spherical geometry assumed, $\mu R = 0.32$).

Determination and Refinement of the Structure

The nickel atom is required by space group symmetry to lie at an inversion center and was placed at the origin. The positions of the Cl and S atoms were located from a sharpened three-dimensional Patterson map. The carbon atom positions were determined from a three-dimensional electron density map phased by the heavy atoms.

A least-squares refinement[16] obtained by using the atomic positions determined from the Fourier map and isotropic temperature coefficients of $B = 4.0$ Å^2 for all nonhydrogen atoms gave an R $(\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.22. Two least-squares iterations were carried out with the isotropic temperature coefficients. Anisotropic temperature coefficients were included in the next two iterations, yielding a final discrepancy index of $R = 0.046$. A difference Fourier map computed at this stage showed regions of significant residual electron density near the C(2) position. The large value of the C(1)–C(2)–C(3) angle (137°), the short C–C bonds to C(2), and the positions of small maxima near C(1) and C(3), presumed to be caused by disordered H atoms, also indicated disorder of C(2). However, apart from the disorder features around C(2) (and similar but much less pronounced effects at C(5)) the difference map showed no disturbing features, and the H atoms at C(4), C(5), and C(6) were clearly indicated.

An attempt to refine the structure with C(2) disordered did not meet with success, and we terminated refinement at the point indicated above, since any additional information that might be gained about the disorder and the hydrogen atom parameters from further refinement would have little bearing on the structural problem we set out to solve.

The positional coordinates and anisotropic temperature factors, together with estimated standard deviations, are given for the Ni, Cl, S, and C atoms in Table I.

Table II. Interatomic Distances (Å)

Bonding

Ni–S(1)	2.478 (3)	S(1)–C(1)	1.807 (11)	C(1)–C(2)	1.44 (3)
Ni–S(2)	2.497 (3)	S(1)–C(6)	1.805 (13)	C(2)–C(3)	1.38 (3)
Ni–Cl	2.358 (3)	S(2)–C(3)	1.812 (16)	C(4)–C(5)	1.50 (3)
		S(2)–C(4)	1.805 (16)	C(5)–C(6)	1.51 (2)

Nonbonding

S(1)–S(2) (intramolecular)	3.335 (3)
S(1)–S(2) (intermolecular)	3.481 (3), 3.554 (3)

Table III. Intramolecular Angles (deg)

S(1)–Ni–S(2)	88.8 (1)	C(1)–S(1)–C(6)	103.3 (7)
S(1)–Ni–Cl	85.9 (1)	C(3)–S(2)–C(4)	102.2 (9)
S(2)–Ni–Cl	87.2 (1)		
		S(1)–C(1)–C(2)	119.6 (13)
Ni–S(1)–C(2)	107.9 (4)	S(1)–C(6)–C(5)	115.0 (11)
Ni–S(1)–C(6)	112.6 (4)	S(2)–C(3)–C(2)	123.5 (16)
Ni–S(2)–C(3)	111.2 (5)	S(2)–C(4)–C(5)	117.6 (11)
Ni–S(2)–C(4)	108.3 (5)		
		C(1)–C(2)–C(3)	137.1 (22)
		C(4)–C(5)–C(6)	120.4 (15)

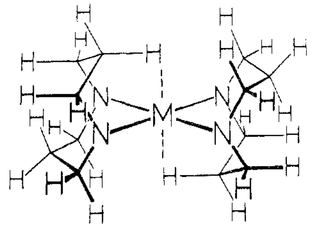

Figure 1. Favored conformation of 1,5-diazacyclooctane in square-planar complexes.

Description of the Structure

The unit cell contains two formula units: two nickel atoms, four chlorine atoms, and four 1,5-dithiacyclooctane (dtco) molecules. When nickel atoms are placed at the corners of the unit cell, another nickel atom lies at the center of the unit cell. The nickel atoms are bridged by dtco ligand molecules (the two sulfur atoms in each dtco molecule are bonded to different nickel atoms) forming a two-dimensional network of interconnecting nickel atoms perpendicular to the [1,0,−1] vector (see Figure 2). The planes of the networks are separated by a distance of half the [1,0,−1] unit cell diagonal. There is no strong chemical bonding between these layers.

The geometry of the donor atoms around the nickel atom is octahedral (see Figure 3). All of the S–Ni–S and S–Ni–Cl bond angles are close to 90° (see Figure 4 and Tables II and III for bond angles and distances).

The sulfur atoms form a parallelogram of an approximately square shape: 3.48 × 3.55 Å. The Ni–Cl distance (2.36 Å) is somewhat shorter than the Ni–S bond distances (2.48 and 2.50 Å).

The ligand molecule assumes a boatlike conformation with a fairly short nonbonding S–S distance of 3.335 Å. The disorder features associated with C(2) mentioned earlier indicate that the ligand adopts both chair-boat and double-chair (or crown) conformations; the C(2) atom can assume two different positions (see Figure 5).

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(16) Full-matrix least-squares refinement of the structure was performed with a revised version (FMLS, by H. Hope) of the program UCLA-LS4 written by P. K. Ganzel, R. A. Sparks, R. E. Long, and K. N. Trueblood. The program minimizes the weighted sum of $(KF_o - G|F_c|)^2$, where K and G are the respective scale factors, G being an adjustable parameter. The weighting scheme used in this structure determination was that of E. W. Hughes, *J. Amer. Chem. Soc.*, 63, 1737 (1941), with $4F_o(\min) = 7.1$. Scattering factors used for Ni, Cl, S, and C in the calculations of F_c were those tabulated by H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

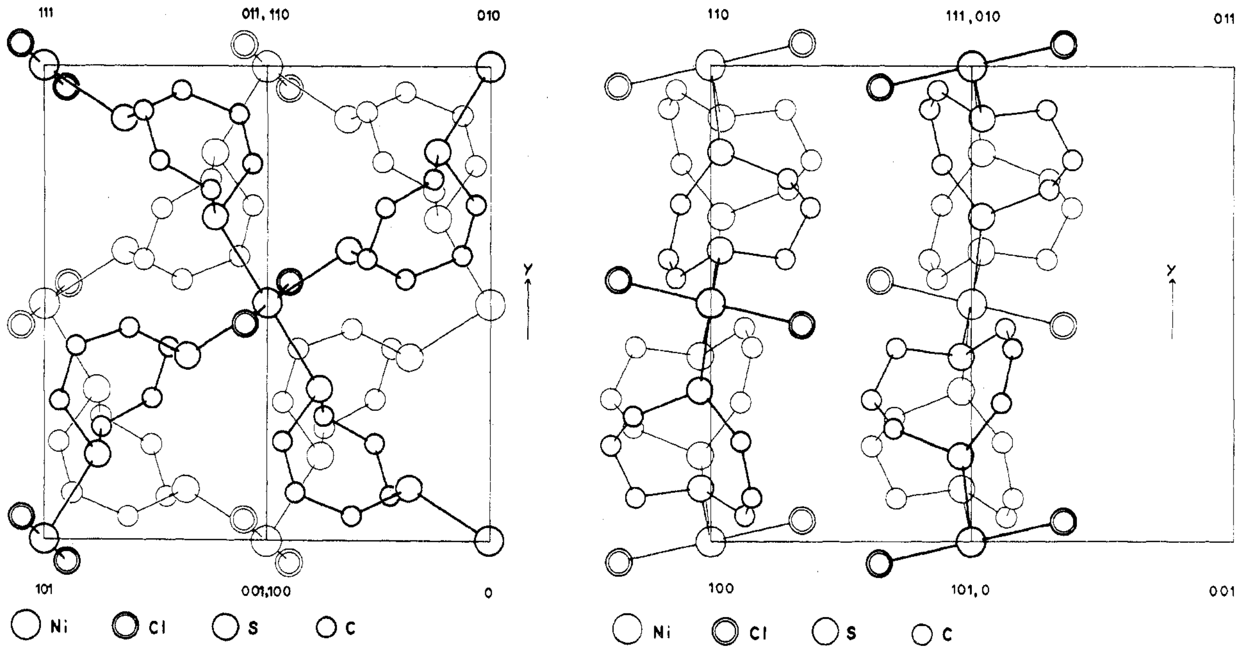

Figure 2. Left: projection of the structure along the [1,0,–1] vector. Right: projection along [1,0,1].

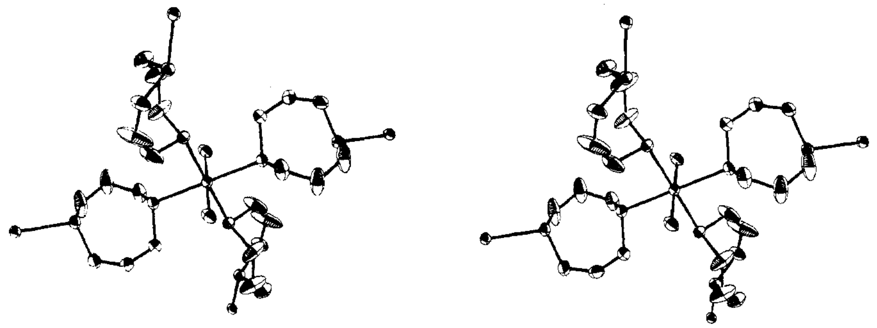

Figure 3. ORTEP diagram. Stereoscopic view of the complex.

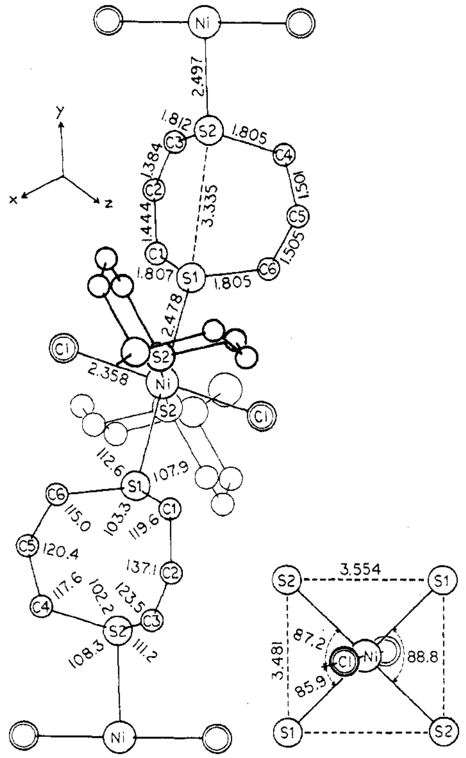

Figure 4. Interatomic distances and bond angles.

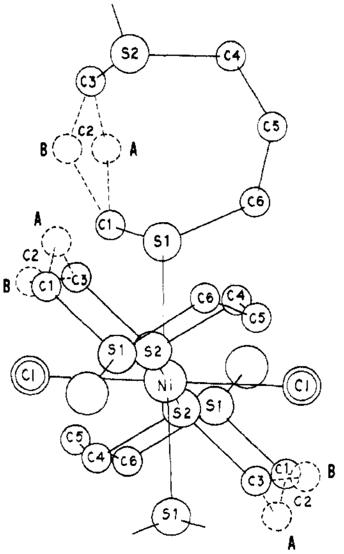

Figure 5. Disorder in the ligand molecule: A, chair–boat conformation; B, double-chair (crown) conformation.

Discussion

Apparently this is the first determination of an octahedral nickel(II) complex containing thioether donors, so direct comparisons of bond lengths and bond angles cannot be made.

The nickel-chlorine bond distance in $Ni(dtco)_2Cl_2$ is shorter than in other octahedral nickel complexes containing axial chlorine atoms by 0.03-0.16 Å,[17-19] probably due to the weak bonding of the thioether donor.

The nickel-thioether sulfur distance in the binuclear square-planar complex Ni_2 [bis(2-mercaptoethyl) sulfide]$_2$[20] is much shorter (by 0.34 Å) than the nickel-sulfur distances in $Ni(dtco)_2Cl_2$, due not only to the smaller number of bonds to the nickel atom but also to the thioether donor being held closely to the nickel atom by ligand strain. The nickel-sulfur distances in $Ni_2(dtco)_2Cl_2$ are much longer (by about 0.33 Å) than in square-planar complexes containing saturated thiolate complexes[20,21] and are about the same length as in thioketone complexes (2.46 Å[18] and 2.51 Å[22]). There appears to be close contact, and therefore repulsion, between the chlorine atom and ligand hydrogen atoms in $Ni(dtco)_2Cl_2$ which probably results in longer nickel-sulfur distances than would be expected in thioether complexes which lack similar repulsions.

The sulfur-carbon distances in $Ni(dtco)_2Cl_2$ (1.81 Å) are typical of single S-C bonds found in sulfur-containing transition metal complexes (1.80-1.87 Å[20,21,23,24]) and in uncomplexed dithiane (1.80, 1.82 Å[25]).

S-C-C (115-124°) and C-S-C (102, 103°) angles are close to those measured in other thioether complexes[23,24] and in dithiane[25] (108-117° for S-C-C and 95-102° for C-S-C). The measured C-C-C angles are much larger than the tetrahedral angle, most of this effect presumably being caused by the disorder described above. Some ligand strain may also be involved: the C-C-C angles in 1,5-diazacyclooctane-*N,N'*-diacetatoaquonickel(II) dihydrate are about 116°.[6]

X-Ray powder diffraction spectra show that $Ni(dtco)_2Cl_2$ is not isomorphous with any nickel(II) or copper(II) complexes studied to date.[5] However, $Ni(dtco)_2I_2$ may have a similar structure, since in this diamagnetic complex the presence of charge-transfer bands indicate nickel-iodide bonding, but the iodide ion probably could not get close enough to the metal to coordinate if the ligands were chelated. The observation of bridging dtco ligands in this complex also helps to justify the prediction of bridging dtco ligands in $Ni_2(dtco)_3Br_4$.[5]

The chair-boat form of dtco found in $Ni(dtco)_2Cl_2$ is probably very similar to the form it takes in complexes in which it acts as a chelating agent. Only a slight increase in the S-S intraligand distance (3.335 Å) is required to achieve chelation: the smallest S-S distance in the NiS_4 plane is 3.48 Å (Figure 3).

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Registry No. $Ni(dtco)_2Cl_2$, 36006-24-3.

Supplementary Material Available. Table IV, a listing of the observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-2079.

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Crystal and Molecular Structure of Δ-[$\overline{\mathrm{PtCl}\{o\text{-}(\mathrm{C_6H_5})_2\mathrm{PC_6H_4C}}\mathrm{=CHC_6H_4P(C_6H_5)_2}\text{-}o\}$]

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The crystal and molecular structure of Δ-{*trans*-1,2-bis[*o*-(diphenylphosphino)phenyl]ethenyl}chloroplatinum(II), Δ-[PtCl{*o*-$(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2$-*o*}], has been determined by three-dimensional X-ray structural analysis using data collected by counter methods. The complex crystallizes in the acentric monoclinic space group $P2_1$ ($C_2{}^2$, No. 4), with $a = 10.633$ (4) Å, $b = 16.934$ (6) Å, $c = 9.957$ (4) Å, $\beta = 119.02$ (2)°, $Z = 2$, $\rho_{\text{obsd}} = 1.64$ (1) g cm^{-3}, and $\rho_{\text{calcd}} = 1.65$ g cm^{-3}. The structure was solved by conventional Patterson and Fourier techniques and was refined by block-diagonal least-squares methods to final weighted and unweighted R factors of 0.040 and 0.042, respectively, for the 4872 unique reflections ($hk\pm l$ and $h\bar{k}\pm l$) with $I/\sigma(I) \geqslant 3.0$. The coordination at the central platinum atom is essentially square planar. The two phosphorus atoms of the novel tridentate ligand *o*-$(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2$-*o*, are trans, and the Pt–P distances [2.266 (3) and 2.269 (3) Å] are equal within experimental error (3.0σ). The chlorine atom [Pt–Cl = 2.377 (2) Å] is trans to the σ-bonded carbon atom [Pt–C = 2.016 (8) Å], and as expected, there is a marked structural trans effect. The olefinic carbon–carbon distance is 1.336 (12) Å.

Introduction

The ligand 2,2'-bis(diphenylphosphino)bibenzyl (I) loses two benzylic hydrogen atoms on reaction with rhodium(I)-chloro complexes or rhodium(III) chloride, to give chlororhodium(I) complexes of the corresponding trans stilbene ligand *o*-$(C_6H_5)_2PC_6H_4CH{=}CHC_6H_4P(C_6H_5)_2$-*o* (II).[1] In