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References and Notes

(1) For example, G. N. Schrauzer, G. W. Kiefer, K. Tano, and P. A. Doemeny, *J. Amer. Chem. Soc.*, **96**, 641 (1974).
(2) G. W. Parshall, *J. Amer. Chem. Soc.*, **87**, 2113 (1965); (b) *ibid.*, **89**, 1822 (1967); (c) *Inorg. Syn.*, **12**, 26 (1970).
(3) S. D. Ittel and J. A. Ibers, *J. Amer. Chem. Soc.*, **96**, 4804 (1974).
(4) S. Krogsrud, S. D. Ittel, and J. A. Ibers, Abstract E1, American Crystallographic Association Meeting, Aug 1974.
(5) H. F. Klein and J. F. Nixon, *Chem. Commun.*, 42 (1971).
(6) S. D. Ittel and J. A. Ibers, *J. Organometal. Chem.*, **57**, 389 (1973).
(7) S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, in press.
(8) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).
(9) In addition to various local programs for the CDC 6400, computer programs used in this work include local versions of Zalkin's FORDAP Fourier program, the AGNOST absorption program, and Busing and Levy's ORFFE function and error program. Our least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program.
(10) "International Tables for X-Ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, 1974.
(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(12) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(13) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).
(14) See paragraph at end of paper regarding supplementary material.
(15) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).
(16) Typical distances run from 2.28 Å for little trans influence to 2.43 Å for a strong trans influence. See ref 3.
(17) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N.Y., 1968.
(18) R. G. Little and J. A. Ibers, *J. Amer. Chem. Soc.*, **96**, 4440 (1974).
(19) F. R. Hartley, "The Chemistry of Platinum and Palladium," Wiley, New York, N.Y., Appendix II.
(20) A. Ferrari, A. Braibanti, G. Bigliardi, and M. Lanfredi, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **122**, 259 (1965).
(21) Y. Morino, T. Iijima, and Y. Murata, *Bull. Chem. Soc. Jap.*, **33**, 46 (1960).
(22) A. Yamaguchi, I. Ichishima, T. Shimanouchi, and T. Shimanouchi, *Spectrochim. Acta.*, **16**, 1471 (1960).

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Synthesis of Diiminosuccinonitrile Complexes. Preparation and Structure of Bis(diiminosuccinonitrilo)platinum(II) *trans*-Dichlorobis(benzonitrile)platinum(II)

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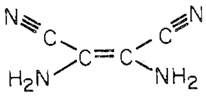
Received August 21, 1974 AIC405976

The complex bis(diiminosuccinonitrilo)platinum(II), [Pt(DISN)$_2$], and the analogs [Pd(DISN)$_2$] and [Ni(DISN)$_2$] have been prepared by the reaction in aqueous solution of the appropriate divalent metal halide with diaminomaleonitrile, oxygen, and a base. The reaction of diiminosuccinonitrile with bis(cyclooctadiene)nickel(0) also yields [Ni(DISN)$_2$]. [Pt(DISN)$_2$] can be prepared from $PtCl_4$, diaminomaleonitrile, and a base. An unusual material [Pt(DISN)$_2$][$PtCl_2(C_6H_5CN)_2$] has been prepared by mixing stoichiometric quantities of the two components. The structure of this material has been determined from three-dimensional X-ray data collected by counter methods. The space group is C_{2h}^3-$C2/m$ with $a = 23.274$ (6) Å, $b = 12.439$ (3) Å, $c = 4.480$ (2) Å, $\beta = 98.68$ (1)°, $Z = 2$, $\rho_{\text{measd}} = 2.28$ (1) g/cm^3, and $\rho_{\text{calcd}} = 2.278$ g/cm^3. The structure has been refined by full-matrix least-squares techniques to a conventional R index (on F) of 0.029 for the 734 reflections with $F_o^2 > 3\sigma(F_o^2)$. The material consists of independent [Pt(DISN)$_2$] and [$PtCl_2(C_6H_5CN)_2$] molecules. The planar molecules form separate columns with interplanar distances of about 3.40 Å. The columns are held together by hydrogen bonds between the molecules. The bond distances found within the [Pt(DISN)$_2$] molecule suggest that the ligand has a delocalized electronic structure and that the compound is best described as a platinum(II) complex.

Introduction

Square-planar transition metal complexes with unsaturated electron-rich ligands are of considerable interest. Since such ligands alter the normal electronic environments of transition metals, these transition metal complexes have unusual properties, including spectroscopic, magnetic, and redox. Included among these interesting compounds are numerous complexes containing ligands with sulfur donors (dithiolates),[1-3] nitrogen or oxygen donors,[3-7] and, more recently, carbon donors.[8]

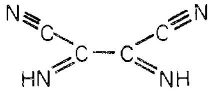
One ligand which can serve potentially in such a manner is diaminomaleonitrile (DAMN). This ligand, which is a substituted olefin, is electron rich and can coordinate to a metal in a number of different ways.



DAMN

Miles, *et al.*,[9] have shown that DAMN will react with Na_2PdCl_4 in acidic solution to give *trans*-dichlorobis(diaminomaleonitrile)palladium(II). The DAMN ligand serves as a monodentate amine and the complex has a trans square-planar geometry as deduced from an X-ray study. In addition, brief mention was made of the preparation in basic solution of neutral complexes of Ni(II), Pd(II), and Pt(II), which contain two DAMN molecules as the only ligands. These neutral complexes were thought to be analogs of the well-characterized metal complexes formed by the reaction of *o*-phenylenediamine with a variety of divalent metal halides in basic solution.[4,5] The *o*-phenylenediamine-derived complexes are formally complexes of the anion of benzoquinonediimine (BQDI). The complexes [M(BQDI)$_2$] (M = Co, Ni, Pd, or Pt) are intensely colored, have an extensive electrochemistry, and are themselves analogs of certain dithiolate complexes where the N–H group of the ligand is replaced by a sulfur atom.[4]

We find, on the basis of the details reported here, that these neutral complexes prepared from DAMN can be described as complexes of the anion of diiminosuccinonitrile (DISN).



DISN

The complexes [M(DISN)$_2$] (M = Ni, Pd, or Pt) have an intense blue or green color and are analogs of the well-known metal complexes of maleonitriledithiol (MNT).[1,2]

We wish to report greatly improved synthetic methods for the preparations of the DISN complexes and to report the molecular structure of [Pt(DISN)$_2$]. In an attempt to synthesize [Pt(DISN)$_2$] in a greater yield we used *cis*-dichlorobis(benzonitrile)platinum(II), [$PtCl_2(C_6H_5CN)_2$], as a starting material.[10] The desired product resulted from the reaction, but in addition a few crystals appeared as small copper-colored needles in the reaction mixture. We subjected these crystals to X-ray analysis and found that [Pt(DISN)$_2$], the product of the reaction, had cocrystallized with the trans isomer of the reactant [PtCl$_2$(C$_6$H$_5$CN)$_2$] to form [Pt(DISN)$_2$][PtCl$_2$(C$_6$H$_5$CN)$_2$]. Thus we report the molecular structures of [Pt(DISN)$_2$] and *trans*-[PtCl$_2$(C$_6$H$_5$CN)]. The unusual crystal packing, with resultant close intermolecular contacts, is also discussed.

Experimental Section

Preparations. Diaminomaleonitrile (DAMN) and diiminosuccinonitrile (DISN) were purchased from PCR, Inc.

[Pt(DISN)$_2$]. Method 1. An aqueous solution (200 ml) of K$_2$PtCl$_4$ (0.415 g, 1 mmol) was stirred in an open beaker with DAMN (0.216 g, 2 mmol) for 72 hr. The intensely green precipitate which formed was filtered and washed with H$_2$O and cold ethanol. The crude yield was 70–80%. The product can be purified by recrystallization from acetone.

Method 2. A methanol solution (40 ml) of PtCl$_4$ (0.336 g, 1 mmol) and DAMN (0.216 g, 2 mmol) was stirred and 1 ml of triethylamine was added. After 2 hr the solvent was removed and the resulting solid was slurried in 20 ml portions of water to remove excess amine. The yield of crude solid was about 50%. *Anal.* Calcd for C$_8$H$_4$N$_8$Pt: C, 23.59; H, 0.98; N, 27.52. Found: C, 23.48; H, 1.10; N, 27.38.

[Pd(DISN)$_2$]. This compound was prepared by the method of Miles, *et al.*[9] The yield was very low, 2–5%. *Anal.* Calcd for C$_8$H$_4$N$_8$Pd: C, 30.16; H, 1.26; N, 35.17. Found: C, 30.40; H, 1.30; N, 34.95.

[Ni(DISN)$_2$]. Method 1. This compound was prepared by the method of Miles, *et al.*,[9] using triethylamine as the base. The yield was 10–15%.

Method 2. Bis(cyclooctadiene)nickel(0)[11] (0.275 g, 1 mmol) was dissolved in 20 ml of benzene under an argon atmosphere. DISN (0.212 g, 2 mmol) dissolved in ethanol was slowly added to the benzene solution. An intense green color developed immediately. The solvent was removed yielding pure Ni(DISN)$_2$ in essentially quantitative yield. *Anal.* Calcd for C$_8$H$_4$N$_4$Ni: C, 35.47; H, 1.49; N, 41.36. Found: C, 35.60; H, 1.54; N, 41.26.

[Pt(DISN)$_2$][PtCl$_2$(C$_6$H$_5$CN)$_2$]. Method 1. This material was originally prepared accidentally. A solution of DAMN in 20 ml of CH$_3$OH was added to *cis*-[PtCl$_2$(C$_6$H$_5$CN)$_2$] in 20 ml of CHCl$_3$. The mixture was stirred in an open beaker for 24 hr. The resultant green precipitate was filtered. The chief product was Pt(DISN)$_2$, 20% yield, but in addition a number of copper-colored needles formed. These needles are shown here to be [Pt(DISN)$_2$][PtCl$_2$(C$_6$H$_5$CN)$_2$].

Method 2. Pt(DISN)$_2$ was dissolved in a minimum amount of hot CH$_3$OH. A solution of *cis*-[PtCl$_2$(C$_6$H$_5$CN)$_2$] in hot CHCl$_3$ was added, the mixture was allowed to cool slowly, and long copper-colored needles of the product formed. If the solvent is removed the yield is quantitative. *Anal.* Calcd for C$_{22}$Cl$_2$H$_{14}$N$_{10}$Pt$_2$: C, 30.04; H, 1.60; N, 15.93. Found: C, 30.15; H, 1.70; N, 15.80.

[Ni(DISN)$_2$][PtCl$_2$(C$_6$H$_5$CN)$_2$] and [Pd(DISN)$_2$][PtCl$_2$(C$_6$H$_5$CN)$_2$]. These materials may be prepared in a manner analogous to method 2 for the Pt compound. *Anal.* Calcd for C$_{22}$Cl$_2$H$_{14}$N$_{10}$NiPt: C, 35.56; H, 1.90; N, 18.85. Found: C, 35.75; H, 2.01; N, 18.6. *Anal.* Calcd for C$_{22}$H$_{14}$Cl$_2$N$_{10}$PdPt: C, 33.41; H, 1.78; N, 17.71. Found: C, 33.59; H, 1.95; N, 17.50.

The magnetic susceptibilities of all compounds were measured on a Faraday balance. The X-ray photoelectron spectra were taken on an AEI EX 100B spectrometer using a technique described previously.[12] The apparatus used for conductivity measurements of pressed pellets has been described elsewhere.[13]

X-Ray Structure Determination. Crystals of what proved to be [Pt(DISN)$_2$][PtCl$_2$(C$_6$H$_5$CN)$_2$] are very thin needles and are quite fragile. Preliminary film work indicated that the crystals are monoclinic and that possible space groups are $C2/m$, $C2$, or Cm. In addition, reflections with $h + k + l = 2n$ were found to be systematically stronger than those with $h + k + l = 2n + 1$. This suggested that the Pt atoms in the cell form a face-centered array. The density of the crystals, determined by flotation methods, was 2.28 (1) g/cm^3 and the value calculated for 2 formula units in the cell is 2.278 g/cm^3.

The crystal selected for data collection was a needle with the approximate dimensions 0.49 × 0.03 × 0.06 mm. The lattice parameters were obtained as previously described.[14] Hand centering of 15 reflections with Mo Kα_1 radiation (λ 0.70930 Å) in the range $25° \leq 2\theta \leq 28°$ yielded the cell parameters a = 23.274 (6) Å, b = 12.439 (3) Å, c = 4.480 (2) Å, and β = 98.68 (1)°.

Data were collected in shells of 2θ by the θ–2θ scan method using Mo Kα radiation monochromatized from the (002) face of a mosaic graphite crystal. The scan range was from 1° below the Mo Kα_1 peak to 1° above the Mo Kα_2 peak and the scan rate was 1°/min. The takeoff angle was 2.4° and the counter was positioned 31 cm from the crystal with an aperture 6.5 mm high by 6.5 mm wide. Data (k, $l \geq 0$) were collected in the range $3° \leq 2\theta \leq 52°$ with backgrounds of 10 sec for $2\theta \leq 35°$, 20 sec for $35° \leq 2\theta \leq 42°$, and 100 sec for $2\theta > 42°$. In addition data for k, $l < 0$ were collected out to 35°. The intensities of 6 standard reflections, which were monitored every 100 reflections, showed only the expected statistical variation. Data collection was terminated at 52° owing to a lack of a significant number of reflections above background. The data were processed in the usual manner,[14,15] using a value of 0.04 for p.

The chemical composition of the crystals was initially unknown. However, the unusual intensity pattern observed photographically suggested that the Pt atoms are in a face-centered array. A structure factor calculation with Pt atoms at special positions (0, 0, 0) and (0, $^1/_2$, $^1/_2$) in $C2/m$ was followed by a difference Fourier calculation which revealed the positions of the remaining atoms. With the composition now established, the data were next corrected for absorption, the transmission coefficients ranging from 0.452 to 0.726 (μ = 117 cm^{-1}).[15] The 420 Friedel pairs were compared and found to deviate an average of 1.7% from their average values. This is a good indication that the correct space group is the centric one, C_{2h}^3-$C2/m$. Therefore Friedel pairs were averaged and combined with the high-angle data to yield 734 unique reflections with $F^2 > 3\sigma(F^2)$. These data were used in subsequent refinements. In $C2/m$ both the [Pt(DISN)$_2$] and [PtCl$_2$(C$_6$H$_5$CN)$_2$] molecules have crystallographically imposed symmetry $2/m$.

The structure was refined by full-matrix least-squares techniques. The quantity minimized is $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes and where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Values of the atomic scattering factors and the anomalous terms were taken from the usual sources.[16]

Initial refinement using isotropic thermal parameters led to values of R and R_w of 0.140 and 0.154. When anisotropic thermal parameters were introduced for the Pt and Cl atoms R and R_w were reduced to 0.049 and 0.061. In this refinement the phenyl ring was treated as a rigid group with D_{6h} symmetry (C–C bond length of 1.392 Å). Next, all nongroup atoms were allowed to vibrate anisotropically, and R and R_w were reduced to 0.034 and 0.038. Hydrogen atoms were located in a difference Fourier map. Those for the phenyl group were idealized (C–H = 1.0 Å, B(H) = B(C) + 1.0 Å^2). These hydrogen atoms were added as fixed contributions to the structure factors in the final cycles of refinement. The refinement converged to values of R and R_w of 0.029 and 0.030. A further refinement based on F^2 was carried out using all of the 1475 unique reflections. The results of the refinement on F are reported here, as refinement on F^2 did not significantly reduce the errors on the parameters. These errors are necessarily large, as the scattering is dominated by the Pt atoms in special positions.

An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of setting angles, $|F_o|$, and Miller indices shows no unusual trends. The standard deviation of an observation of unit weight is 0.76 electron, based on the 62 variables and 734 observations. A structure factor calculation for the 748 reflections having $F_o^2 < 3\sigma(F_o^2)$, which were omitted from the refinement, showed no reflections having $|F_o^2 - F_c^2| > 2\sigma(F_o^2)$. These 748 reflections are omitted from Table I where the values of $10|F_o|$ and $10|F_c|$ are given.[17] The final atomic parameters for the nongroup atoms are listed in Table II. The group parameters are listed in Tables III. The root-mean-square amplitudes of vibration are listed in Table IV.

Description of the Structure

The Crystal Structure. The crystal structure consists of independent [Pt(DISN)$_2$] and [PtCl$_2$(C$_6$H$_5$CN)$_2$] molecules. The two independent molecules stack in separate columns parallel to the short axis, c. This packing may be seen both

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $[Pt(DISN)_2][PtCl_2(C_6H_5CN)_2]^b$

Atom	x^a	y	z	β_{11} or B, Å^2	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt(1)	0	$^1/_2$	$^1/_2$	2.26 (4)	3.86 (7)	53.7 (11)	0	3.18 (16)	0
Pt(2)	0	0	0	1.99 (3)	3.59 (7)	56.5 (11)	0	3.90 (16)	0
Cl	0	0.1821 (3)	0	4.16 (14)	4.03 (24)	132 (5)	0	3.7 (7)	0
N(1)	0.0507 (3)	0.3998 (5)	0.7531 (19)	2.44 (21)	3.5 (5)	49 (6)	0.84 (26)	1.0 (9)	5.3 (14)
N(2)	0.1586 (4)	0.3310 (7)	0.3324 (29)	3.5 (3)	6.5 (7)	103 (10)	0.3 (4)	2.4 (14)	−0.3 (23)
N(3)	0.0665 (6)	0	−0.678 (3)	2.3 (3)	6.8 (10)	47 (9)	0	0.9 (15)	0
C(1)	0.0916 (5)	0.4431 (7)	−0.0454 (29)	2.58 (29)	5.0 (8)	61 (8)	−0.1 (4)	3.5 (13)	−1.7 (20)
C(2)	0.1290 (5)	0.3807 (9)	0.165 (3)	2.8 (3)	5.5 (8)	87 (11)	−0.2 (4)	6.3 (16)	0.9 (24)
C(3)	0.1041 (8)	0	−0.500 (4)	2.4 (4)	6.5 (13)	45 (11)	0	2.9 (17)	0
H-N(1)	0.049	0.316	0.775	6.0					
H-C(5)	0.157	0.167	−0.218	5.7					
H-C(6)	0.233	0.167	0.209	7.3					
H-C(7)	0.271	0	0.423	7.6					

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are thermal coefficients $\times 10^3$.

Table III. Derived Parameters for the Rigid-Group Atoms of $[Pt(DISN)_2][PtCl_2(C_6H_5CN)_2]^a$

Atom	x	y	z	B, Å^2
C(4)	0.1518 (4)	0	−0.2625 (29)	4.4 (3)
C(5)	0.1754 (4)	0.0973	−0.1458 (23)	5.3 (3)
C(6)	0.2226 (4)	0.0973	0.0877 (18)	5.7 (3)
C(7)	0.2462 (4)	0	0.2044 (19)	6.2 (4)

[a] The rigid-group origin has fractional coordinates 0.1990 (3), 0, −0.0291 (2). The orientation angles of the group δ, ϵ, and η are π, π, and −0.682 (7) radians. The angles have been defined previously: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965).

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Pt(1)	0.174 (2)	0.217 (2)	0.254 (2)
N(1)	0.133 (14)	0.237 (12)	0.262 (11)
C(1)	0.194 (16)	0.234 (16)	0.271 (16)
C(2)	0.204 (16)	0.242 (16)	0.315 (19)
N(2)	0.224 (13)	0.305 (14)	0.321 (15)
Pt(2)	0.167 (2)	0.202 (2)	0.255 (2)
Cl	0.178 (5)	0.333 (6)	0.362 (7)
N(3)	0.216 (21)	0.232 (18)	0.252 (18)
C(3)	0.203 (23)	0.226 (22)	0.256 (23)

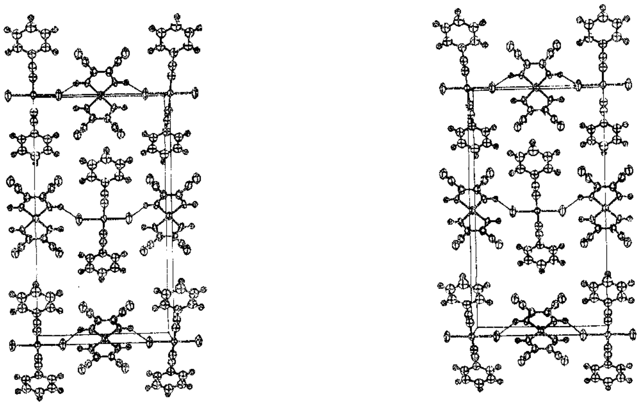


Figure 1. Stereoscopic view of the unit cell of $[Pt(DISN)_2][PtCl_2(C_6H_5CN)_2]$. The x axis is vertical, the y axis is horizontal, and the z axis points out of the paper. The hydrogen-bonding scheme has been drawn. The shapes of the atoms in this and the following drawings represent 50% probability contours of thermal motion. The H atoms are of arbitrary size.

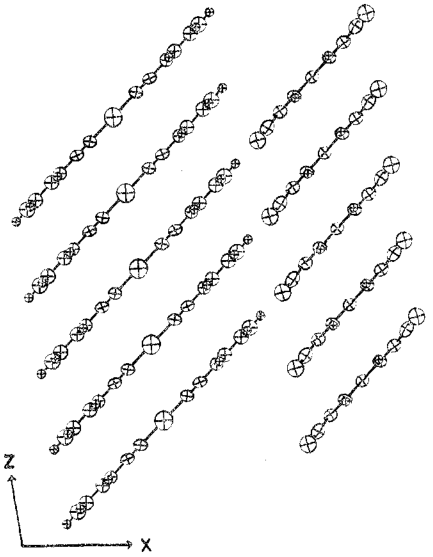


Figure 2. A perspective view of $[Pt(DISN)_2][PtCl_2(C_6H_5CN)_2]$ looking along the y axis. The column on the left contains the $[PtCl_2(C_6H_5CN)_2]$ molecules and the column on the right contains the $[Pt(DISN)_2]$ molecules.

in Figure 1, which is a stereoscopic view of the unit cell, and in Figure 2, which shows an edge-on view of the columns.

The molecules of one column are very nearly coplanar with the independent molecules in the neighboring column (dihedral angle 2.8°). This can be seen in Figure 2. The phenyl groups of the benzonitrile complex point between the cyano groups of the $[Pt(DISN)_2]$ molecule in what may be called a "lock and key" arrangement (Figure 1).

Both sets of independent planar molecules are separated by 3.40 Å. This 3.40-Å interplanar spacing is expected from the van der Waals radius of aromatic carbon atoms and is comparable to interplanar distances found in many aromatic systems.[18] A similar structure is that of platinum phthalocyanine, which has parallel planes with a spacing of 3.38 Å.[19] The closest intermolecular distance between atoms within a column is 3.54 (2) Å, the distance between Pt(2) of the benzonitrile complex and atom C(3) of the benzonitrile cyano group of the molecule above it in the column. The triple bonds of the cyano groups are located in what would be the fifth and sixth coordination positions of Pt(2).

The $[Pt(DISN)_2]$ molecules stack in a similar manner with Pt(1) directly under the bond between C(1) and C(1)′. This bond is a double bond in unliganded DAMN, but as discussed below, it is now intermediate between a double and a single bond. The C(1)···Pt(1) intermolecular distance is 3.55 (2) Å. The shortest Pt···Pt distance is 4.480 (2) Å along the c axis.

The columns of diverse molecules are held together by N-H···Cl bonds between the hydrogen atoms on the imine nitrogen atoms and the chlorine atoms of the benzonitrile complex. Each chlorine atom is involved in two hydrogen bonds. The Cl···N(1) distance is 3.216 (9) Å, well within the hydrogen-bonding range.[20] The hydrogen atom, though found in a difference Fourier map, was not refined. The bond

Table V. Interatomic Distances (Å) and Angles (deg) in $[PtCl_2(C_6H_5CN)_2]$

Pt(2)–Cl	2.265 (5)	Cl–Pt(2)–N(3)	90
Pt(2)–N(3)	1.950 (15)	Pt(2)–N(3)–C(3)	179.3 (14)
N(3)–C(3)	1.091 (20)	N(3)–C(3)–C(4)	178.2 (19)
C(3)–C(4)	1.418 (20)	C(3)–C(4)–C(5)	120.0 (4)
C(4)–C(5) = C(5)–C(6) = C(6)–C(7) (rigid group)	1.397		

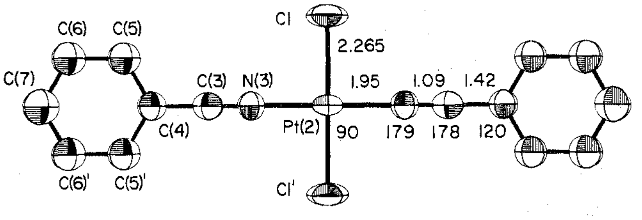


Figure 3. The $[PtCl_2(C_6H_5CN)_2]$ molecule.

parameters based on this crude positioning are N(1)–H = 1.05 Å, Cl···H = 2.33 Å, and Cl···H–N(1) = 141°.

The $[PtCl_2(C_6H_5CN)_2]$ Molecule. The benzonitrile complex $[PtCl_2(C_6H_5CN)_2]$ has been studied extensively and is a widely used starting material for preparation of organometallic complexes of platinum.[10] The complex has been assigned a cis configuration on the basis of its dipole moment[21] and its infrared spectrum.[22] The cis and trans isomers of the bromo complex $[PtBr_2(C_6H_5CN)_2]$ presumably have similar stabilities as they have been crystallized from the same reaction mixture.[23] A partial crystal structure of the palladium complex $[PdCl_2(C_6H_5CN)_2]$ has shown it to have a trans geometry.[24]

In the material studied here the complex $[PtCl_2(C_6H_5CN)_2]$ has cocrystallized with $[Pt(DISN)_2]$ and has a trans geometry. The Pt atom is at a special position of $2/m$ symmetry in the unit cell. The molecule is pictured in Figure 3 and Table V lists the intramolecular bond distances and angles. The benzonitrile ligand is bound to the Pt atom in a linear fashion through the terminal nitrogen atom. The coordination geometry about the Pt atom is required by symmetry to be square planar with all angles 90 and 180°. The phenyl group is essentially coplanar with the plane of the coordination sphere making the entire molecule planar with no atom deviating more than 0.03 Å from the best least-squares plane.

The Pt(2)–N(3) bond distance of 1.950 (15) Å is short and is a reflection of the sp hybridization of the nitrogen atom of the cyano group. The Pt(2)–Cl bond is also short, 2.265 (5) Å. Most Pt^{II}–Cl bond lengths are longer, in the range 2.30–2.33 Å.[25]

The $[Pt(DISN)_2]$ Molecule. The $[Pt(DISN)_2]$ molecule is pictured in Figure 4. Table VI lists the intramolecular bond distances and angles. It is a highly symmetric molecule with crystallographically imposed $2/m$ symmetry. Difference Fourier maps revealed that there is one hydrogen atom bound to each nitrogen atom. The molecule is essentially planar with a maximum deviation of 0.06 Å of atoms from the best least-squares plane. The ligand is thus formally a diiminosuccinonitrile molecule.

Since several resonance forms and corresponding electronic formulations are possible for the molecule, a detailed examination of bond lengths in the ligand is useful.

The average bond lengths found for chemically equivalent bonds in the free DAMN ligand[26] are also listed in Table VI. For $[Pt(DISN)_2]$ the C(1)–C(1)' bond length is 1.416 (19) Å, intermediate between the double bond in free DAMN (1.36 (1) Å) and a single-bond distance (1.49 Å for sp^2 carbon atoms).[26] The N(1)–C(1) bond length of 1.323 (13) Å is intermediate between the single bond (1.39 (1) Å) in DAMN and the double-bond value of 1.28 Å found for various nitrogen-coordinated imine complexes.[25] Since both the N(1)–C(1) and the C(1)–C(1)' bond lengths are intermediate between the lengths expected for single and double bonds, the ligand may be assumed to have a delocalized electronic structure.

Table VI. Bond Distances (Å) and Angles (deg) in $[Pt(DISN)_2]$ and Related Molecules

	$[Pt(DISN)_2]$	DAMN[a]		$[Cu(MNT)_2]^{2-}$ [b]
		Distances		
Pt(1)–N(1)	1.957 (8)		Cu–S	2.267 (2)
N(1)–C(1)	1.323 (13)	1.392 (8)	S–C(1)	1.727 (2)
C(1)–C(1)'[c]	1.416 (19)	1.363 (6)	C(1)–C(1)'	1.362 (4)
C(1)–C(2)	1.415 (15)	1.439 (7)	C(1)–C(2)	1.432 (4)
C(2)–N(2)	1.123 (15)	1.165 (10)	C(2)–N(2)	1.144 (4)
	$[Pt(DISN)_2]$	DAMN[a]		$[Cu(MNT)_2]^{2-}$ [b]
		Angles		
N(1)–Pt(1)–N(1)'	79.1 (5)		S–Cu–S	90.7 (3)
Pt(1)–N(1)–C(1)	116.4 (7)		Cu–S–C(1)	101.6 (3)
N(1)–C(1)–C(1)'	114.0 (6)	124.1 (4)	S–C(1)–C(1)'	122.9 (3)
N(1)–C(1)–C(2)	122.6 (9)	117.6 (3)	S–C(1)–C(2)	117.1 (3)
C(1)–C(1)'–C(2)'	123.3 (7)	118.1 (8)	C(1)–C(1)'–C(2)	120.0 (4)
C(1)–C(2)–N(2)	179.7 (13)	179.8 (9)	C(1)–C(2)–N(2)	179.4 (4)

[a] Average bond distances and angles of corresponding bonds in the free DAMN molecule.[26] [b] Average bond distances and angles found for chemically analogous bonds in $[N(C_2H_5)_4][Cu(MNT)_2]$ and $[N(C_4H_9)_4][Cu(MNT)_2]$.[27] [c] Primed atoms are related to the corresponding unprimed atoms by a mirror plane.

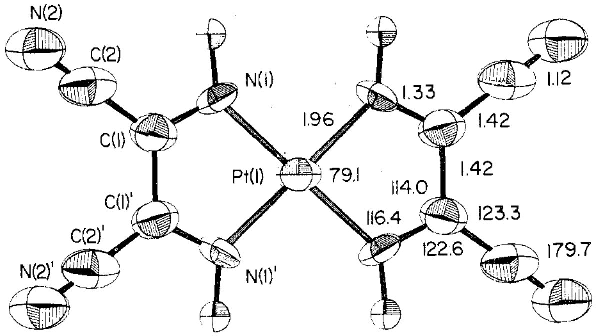


Figure 4. The $[Pt(DISN)_2]$ molecule.

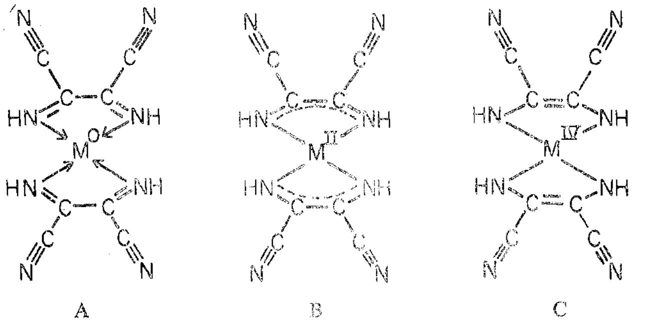
The Pt(1)–N(1) bond distance of 1.957 (8) Å is shorter than most Pt^{II}–N bond lengths but is similar to values found for other platinum–oxime or –imine complexes.[25]

The maleonitriledithiol (MNT) ligand is analogous to DISN in that the N–H group is replaced with an S atom. The MNT complexes are stable in anionic forms. The structures of several of these anionic complexes have been determined.[2] All are very similar to that of $[Pt(DISN)_2]$. Table VI also gives the bond distances and angles found for the $[Cu(MNT)_2]^{2-}$ anion.[27] The major structural differences between an MNT complex and the $[Pt(DISN)_2]$ complex result from the larger radius of the sulfur atom. Both complexes are planar and the geometry of the cyano groups is similar.

Discussion

The product of the reaction of diaminomaleonitrile with K_2PtCl_4 has been shown by the X-ray structural investigation to be a square-planar Pt complex of diiminosuccinonitrile. The elemental analyses of the Ni, Pd, and Pt compounds are all consistent with this formulation. The DAMN molecules lose two protons upon coordination and become, in a formal sense, DISN ligands.

Three resonance forms (A–C) can be drawn for the neutral DISN metal (M) complexes. In one extreme (A) the complexes may be thought of as M(0) coordinated to neutral DISN ligands. In the other extreme (C) M(IV) is coordinated to twice deprotonated DAMN ligands. Each of these two



formulations would predict localized double and single bonds within the chelate ring. The results of the X-ray structure determination indicate that the ligand has a delocalized structure. This suggests that the best description is intermediate B: M(II) is coordinated to the anion of DISN, formed by the deprotonation and oxidation of DAMN. All of the DISN complexes are diamagnetic, as expected for square-planar complexes of d^8 transition metals. Thus, the correct name for the Pt complex is bis(diiminosuccinonitrilo)platinum(II).

These complexes can be prepared with Ni, Pd, and Pt as the transition metal. In general, a divalent metal halide is dissolved in an aqueous solution of a suitable base. DAMN is added, and the mixture stirred without exclusion of dioxygen. The platinum compound can be prepared in good yield (70–80%) by this method, the nickel compound in fair yield (10–15%), and the palladium compound in only small yield (2–5%). The reaction of $CoCl_2 \cdot 6H_2O$ with DAMN yields a similar product, but the reaction is complicated by the presence of a Co(III) species. Further studies are in progress.

The reaction of DAMN with a divalent metal chloride involves an oxidation of DAMN and deprotonation, for example

$$NiCl_2 \cdot 6H_2O + 2DAMN + {}^1/{}_2O_2 \rightarrow [Ni(DISN)_2] + 7H_2O + 2HCl$$

A base is added to assist the deprotonation. The reaction does not occur in the absence of dioxygen.

An examination of the different resonance forms for the complexes suggests alternative methods of synthesis. Reaction of the α-diimine DISN with a Ni(0) complex should yield the $[Ni(DISN)_2]$ complex. Indeed, bis(cyclooctadiene)nickel(0), $[Ni(COD)_2]$, reacts with DISN to give $[Ni(DISN)_2]$, *i.e.*

$$[Ni(COD)_2] + 2DISN \rightarrow [Ni(DISN)_2] + 2COD$$

The reaction leads in a much higher yield to a product identical with that prepared previously. This reaction is analogous to that of $[Ni(CO)_4]$ with *o*-benzoquinonediimine to yield $[Ni(BQDI)_2]$.[4] For routine syntheses $[Ni(COD)_2]$ is a much more convenient starting material than the dangerous and hard-to-handle $[Ni(CO)_4]$.

Another method for the synthesis of the Pt compound is suggested by the third resonance form. Indeed if $PtCl_4$ is allowed to react with DAMN in the presence of a base, such as triethylamine, the identical $[Pt(DISN)_2]$ complex forms, *i.e.*

$$PtCl_4 + 2DAMN + NR_3 \rightarrow [Pt(DISN)_2] + 4[HNR_3]Cl$$

This reaction does not require dioxygen unlike the reaction of K_2PtCl_4 with DAMN.

These DISN complexes are examples of anionic α-diimine compounds. There are a number of analogous complexes known. Thus $[M(BQDI)_2]$ (M = Co, Ni, Pd, or Pt) are complexes of the anion of *o*-benzoquinonediimine.[4] The simple α-diimine biacetylbisanil reacts with $[Ni(CO)_4]$ to give a similar compound.[4] Also related are the well-known[28] neutral complexes bis(bipyridyl)nickel(0) and bis(*o*-phenanthroline)nickel(0), which can be formulated as nickel(II) complexes of anionic α-diimine ligands. All such systems are characterized by intense absorption bands in the region 600–800 nm. All have an extensive electrochemistry with stable oxidized or reduced species obtainable in various cases.

The neutral complexes $[M(BQDI)_2]$ (M = Co, Ni, Pd, or Pt) can in general be reduced electrochemically to 1− or 2− charged species and can be oxidized to 1+ and 2+ species.[4] The 1+ cation is isolable as the iodide salt. The $[M(DISN)_2]$ (M = Ni, Pd, or Pt) complexes would be expected to show a similar five-electron-transfer series. The cyano groups would probably have a stabilizing effect on the anionic members of the series and a destabilizing effect on the cationic members of the series. Preliminary studies elsewhere[29] have shown that the neutral Pt compound will undergo a reversible two-step reduction and an irreversible oxidation.

The unusual material whose structure is reported here contains cocrystallized $[Pt(DISN)_2]$ and $[PtCl_2(C_6H_5CN)_2]$ molecules. The preferential cocrystallization of the molecules is probably the result of hydrogen-bonding and favorable crystal-packing forces. The molecules are the correct size and shape to fit together in a very tight packing arrangement. There does not appear to be any formal charge transfer between them. The X-ray photoelectron spectrum of the material shows one sharp peak for Pt (Pt $4f^{5/2}$ binding energy is 74.2 eV) in the range expected (73.8–74.8 eV)[30] for Pt(II) complexes, suggesting both Pt atoms are in their normal environments.

Since the material has a metallic appearance and since there is a 3.40-Å interplanar spacing of the molecules, we thought that the material might have interesting conductivity properties. No conductivity for pressed pellets could be detected at a temperature of 200°. For our apparatus this implies an average conductivity less than 10^{-9} ohm^{-1} cm^{-1}. Owing to the fragile nature of the crystals no single-crystal measurements could be made.

All the materials studied are diamagnetic, except $[Pt(DISN)_2][PtCl_2(C_6H_5CN)_2]$ which shows temperature-independent paramagnetism over the temperature range 78–300°K. This paramagnetism is also field dependent. The magnitude of the susceptibility varies from sample to sample with value of χ_m ranging from 800×10^{-6} to 2000×10^{-6} cgsu. Thus the effect may be associated with an impurity.

Although $[Pt(DISN)_2][PtCl_2(C_6H_5N)_2]$ was originally prepared by accident, it can be prepared quantitatively from stoichiometric amounts of the two components. Similar materials can be prepared by cocrystallizing $[PtCl_2(C_6H_5CN)_2]$ with $[Ni(DISN)_2]$ or $[Pd(DISN)_2]$. Both of these materials have a similar metallic appearance and crystallize as needles or fibers. Their crystal structures are probably analogous to the structure reported here. These materials are diamagnetic. Interestingly the complex *trans*-$[PdCl_2(C_6H_5CN)_2]$[10] does not cocrystallize with any of the DISN complexes.

Acknowledgment. We wish to thank Matthey-Bishop, Inc., for the generous loan of precious metals used in this work. This research was sponsored by the National Science Foundation through the Northwestern University Materials Research Center.

Registry No. $[Pt(DISN)_2]$, 34341-53-2; $[Ni(DISN)_2]$, 34303-07-6; $[Pt(DISN)_2][PtCl_2(C_6H_5CN)_2]$, 53495-24-2; $[Ni(DISN)_2][PtCl_2(C_6H_5CN)_2]$, 53495-25-3; $[Pd(DISN)_2][PtCl_2(C_6H_5CN)_2]$, 53495-26-4; bis(cyclooctadiene)nickel(0), 1295-35-8; *cis*-$[PtCl_2(C_6H_5CN)_2]$, 15617-19-3; DAMN, 1187-42-4.

Supplementary Material Available. Table I, the structure 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 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 AIC405976.

References and Notes

(1) A. Davison, N. Edelstein, R. H. Holm, and A. A. Maki, *J. Amer. Chem. Soc.*, **85**, 2029 (1963).
(2) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).
(3) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 219 (1968).
(4) A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966).
(5) G. S. Hall and R. H. Soderberg, *Inorg. Chem.*, **7**, 2300 (1968).
(6) F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).
(7) A. L. Balch, F. Röhrscheid, and R. H. Holm, *J. Amer. Chem. Soc.*, **87**, 2301 (1965).
(8) A. L. Balch and J. E. Parks, *J. Amer. Chem. Soc.*, **96**, 4114 (1974).
(9) M. G. Miles, M. B. Hursthouse, and A. G. Robinson, *J. Inorg. Nucl. Chem.*, **33**, 2015 (1971).
(10) F. R. Hartley, "The Chemistry of Platinum and Palladium," Wiley, New York, N.Y., 1973, pp 462–463.
(11) S. D. Ittel, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1974.
(12) J. W. Lauher and J. E. Lester, *Inorg. Chem.*, **12**, 244 (1973).
(13) D. Cahen, J. R. Hahn, and J. R. Anderson, *Rev. Sci. Instrum.*, **44**, 1567 (1973).
(14) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967); R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).
(15) In addition to various local programs for the CDC 6400 computer, modified versions of the following programs were employed: Zalkin's FORDAP Fourier summation program, Busing and Levy's ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program. Our full-matrix least-squares program NUCLS, in its nongroup form, closely resembles the Busing–Levy ORFLS program. Our absorption program is AGNOST.
(16) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974, Table 2.2A; D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(17) See paragraph at end of paper regarding supplementary material.
(18) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, p 362.
(19) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 36 (1940).
(20) W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N.Y., 1968, pp 259–265.
(21) K. A. Jensen, *Z. Anorg. Allg. Chem.*, **231**, 365 (1937).
(22) R. D. Gilliard and G. Wilkinson, *J. Chem. Soc.*, 2835 (1964).
(23) R. A. Walton, *Can. J. Chem.*, **46**, 2347 (1968).
(24) J. R. Halden and N. C. Baenziger, *Acta Crystallogr.*, **9**, 194 (1956).
(25) F. R. Hartley, "The Chemistry of Platinum and Palladium," Wiley, New York, N.Y., 1973, pp 490–519.
(26) B. R. Penfold and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 589 (1961).
(27) K. Plumlee and J. A. Ibers, unpublished work.
(28) H. Behrens and A. Muller, *Z. Anorg. Allg. Chem.*, **341**, 124 (1965).
(29) W. Geiger, Southern Illinois University, and M. Suchanski, Northwestern University, personal communication.
(30) D. Cahen, Ph.D. Thesis, Northwestern University, Evanston, Ill., 1973.

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Structure of the Chloroform Adduct of Pentakis(phenyl isocyanide)cobalt(I) Perchlorate, $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$[1]

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Received August 25, 1974 AIC40605I

The structure of $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$ has been determined from three-dimensional X-ray diffraction data collected by counter methods. The coordination geometry around the d^8 Co(I) ion is approximately square pyramidal. The complex is situated on a mirror plane. The apical Co–C bond distance is 1.88 (3) Å; the two independent basal Co–C bond distances average 1.83 (2) Å. The trans C_{basal}–Co–C_{basal} bond angle is 156.5 (10)°. There is no coordination in the position trans to the apical ligand. For a series of five-coordinate complexes of d^8 ions there is a strong correlation between the relative bond lengths of these complexes and the distance of the central metal ion from the basal plane; as the bond lengths become equal, the metal ion moves out of the basal plane. Comparison of the geometries of the cobalt(I) and cobalt(II) pentakis(phenyl isocyanide) complexes gives a direct measurement of the structural effects of a one-electron oxidation–reduction. The yellow, needlelike crystals of $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$ conform to space group $P2_1/m$ (C_{2h}^2) with $a = 10.849$ (8) Å, $b = 17.741$ (14) Å, $c = 11.396$ (9) Å, and $\beta = 121.00$ (3)°; $Z = 2$; $\rho_{calcd} = 1.40$ and $\rho_{obsd} = 1.39$ g/cm^3. The structure has been refined with full-matrix least squares using 647 reflections with $F^2 > 2\sigma(F^2)$ to a final weighted R factor of 8.7%.

Introduction

Isocyanide complexes of cobalt and other transition metals have received much interest in recent years. The general area has been reviewed by Malatesta and Bonati[3] and more recently by Treichel.[4] Of immediate interest are the cobalt(I) and cobalt(II) isocyanide complexes because of their structural relationship to the analogous pentacoordinate cyanide complex $[Co(CN)_5]^{3-}$. Although the dimer of the $[Co(CN)_5]^{3-}$ ion has been known for years and has recently been structurally characterized,[5] the monomer has eluded isolation until very recently.[6] Relatively little structural data are available for a comparison of the isocyanide and cyanide complexes of cobalt. Cotton, Dunne, and Wood have reported the structures of the trigonal-bipyramidal $[Co(CNCH_3)_5]^+$ ion[7] and the corresponding dimer[8] $[Co_2(CNCH_3)_{10}]^{4+}$. More recently, the structure of the cobalt(II) complex $[Co(CNC_6H_5)_5]^{2+}$ has been determined;[9] a discussion of the different forms of the cobalt(II) phenyl isocyanide system is presented in the structure report[9] and elsewhere.[10-13] Structure analysis of the $[Co(CNC_6H_5)_5]^{2+}$ and $[Co(CNC_6H_5)_5]^+$ ions presents an opportunity to follow the structure and bonding changes in these pentacoordinate transition metal complexes as a one-electron oxidation–reduction takes place. For this reason and for the additional comparisons to be made with other pentacoordinate d^8 complexes, the structure of $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$ was undertaken.

Experimental Section

Preparation of $[Co(CNC_6H_5)_5]ClO_4{\cdot}HCCl_3$. All preparative operations involved were carried out under dry nitrogen atmosphere using Schlenk apparatus. All solvents were reagent grade and deaerated with N_2 before use.

A mixture of $[Co(CNC_6H_5)_5](ClO_4)_2$[9,14] (0.139 g, 1.80 × 10^{-4} mol) and Na_2SO_3 (0.024 g, 1.9 × 10^{-4} mol) in an ethanol slurry (20 ml) was stirred for several hours at room temperature. As the reduction of the Co(II) salt proceeded, the blue suspension slowly changed to a clear yellow solution. The reaction mixture was filtered to remove excess Na_2SO_3; the yellow filtrate was reduced in volume by vacuum evaporation and then cooled to −15°. The bright yellow crystalline powder of $[Co(CNC_6H_5)_5]ClO_4$ was collected and dried under N_2 atmosphere.

A small amount of the dry $[Co(CNC_6H_5)_5]ClO_4$ product was