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Crystal and Molecular Structure of Dichloro[bis(2-pyridyl) disulfide]cobalt(II)

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Received October 21, 1975 AIC50754G

The crystal and molecular structure of dichloro[bis(2-pyridyl) disulfide]cobalt(II), $Co(C_{10}H_8N_2S_2)Cl_2$, has been determined by single-crystal x-ray diffraction techniques using counter methods and has been refined by full-matrix least-squares procedures to a final conventional R index of 0.050. The deep blue crystals are triclinic, space group $P\bar{1}$, with $a = 8.132$ (4) Å, $b = 12.075$ (9) Å, $c = 7.823$ (7) Å, $\alpha = 107.30$ (6)°, $\beta = 114.85$ (5)°, $\gamma = 94.47$ (5)°, and two molecules per unit cell. The cobalt(II) ion is coordinated tetrahedrally by two chloride ions and the two pyridyl nitrogen atoms of a single ligand; neither sulfur atom coordinates; a seven-membered $\overline{\mathrm{SCNCoNCS}}$ chelate ring is formed. The Co–N bonds are 2.025 (4) and 2.055 (4) Å, and the Co–Cl distances are 2.238 (2) and 2.253 (2) Å. The coordination angles range from 101 to 118°, the two largest being N–Co–N and Cl–Co–Cl. The C–S bonds are 1.773 (6) and 1.776 (6) Å, and the C–S–S–C torsion angle of 102.2 (3)° is near its expected value, 90°. The S–S bond length of 2.040 (2) Å is somewhat longer than the corresponding distance in the free ligand, 2.016 (2) Å. Although the S–S group lies quite close to the plane of both pyridine rings in the uncoordinated ligand, this planarity is absent in the complex; the two C–C–S–S torsion angles are unequal, 107.2 (5) and 142.3 (5)°, and far from the value in the free ligand, near 0°. It can be observed, in conjunction with results on other complexes of this ligand, that the increased S–S bond length is correlated with the C–C–S–S torsion angle and the presence of coordination but does not depend upon whether that coordination is through a sulfur atom.

Introduction

Crystallographic results have shown that one sulfur atom of an R–S–S–R group can coordinate to Ni(II),[1–3] Fe(III),[4] Cu(II) (although at a long distance),[5] and Cu(I).[6–9] Organic disulfide coordination to other transition metal ions, such as Mn(II),[10] Pd(II),[11] and Co(III),[12] has been reported.

The same ligand used in this work, bis(2-pyridyl) disulfide, was found to complex tetrahedral Cu(I) in two nonequivalent ways within a single-crystal structure;[9] one ligand coordinates through its two pyridyl nitrogen atoms only, while the other coordinates through only one pyridyl nitrogen and one disulfide sulfur atom. In some circumstances, then, an organic disulfide group can compete successfully with a pyridyl nitrogen atom for a transition metal ion coordination site.

The stoichiometry of the 1:1 complex between bis(2-pyridyl) disulfide (L) and $CoCl_2$ and the visible–uv spectrum of the complex which is typical of tetrahedrally coordinated Co(II) indicate that not all of the possible donor groups of the ligand are used. This work was undertaken to learn which groups participate in coordination and to learn the effect of coordination on the geometry of the ligand. In this case, the S–S bond length and the C–S–S–C torsion angle, where each sulfur atom is bonded directly to an unsaturated carbon atom, were of interest. The structure of the ligand itself has been determined[13] for comparison.

Preparation Section

Cobalt perchlorate, hydrated, and bis(2-pyridyl) disulfide were obtained from G. Frederick Smith Co. and Aldrich Chemical Co., respectively. All other chemicals were of reagent grade quality. The laser-Raman (excitation 5145 Å), infrared, and ultraviolet spectra were obtained using Cary 82, Beckman IR-10, and Cary 14 spectrometers, respectively. The elemental analyses were performed by Galbraith Laboratories.

Dichloro[bis(2-pyridyl) disulfide]cobalt(II), $Co(pySSpy)Cl_2$.[14,15] A 0.44-g (0.0010-mol) sample of cobalt perchlorate, hydrated, was dissolved in 40 ml of ethanol. To this solution was added 40 ml of ethanol containing 0.0010 mol of the free ligand bis(2-pyridyl) disulfide. Upon the addition of 10 ml of hot, saturated lithium chloride in ethanol, the initially pink solution immediately became blue. Large blue crystals formed as the solution was allowed to stand overnight at room temperature. Subsequent x-ray examination showed that most crystals were twinned. Anal. Calcd for $CoC_{10}H_8N_2S_2Cl_2$: Co, 16.83; C, 34.30; H, 2.30; Cl, 20.25. Found: Co, 16.78; C, 34.25; H, 2.22; Cl, 20.09. Attempts to prepare the perchlorate complex of Co(II) with this ligand molecule did not lead to an isolatable solid; the addition of chloride was necessary.

Spectroscopic Section

The infrared and visible–uv spectral data of dichloro[bis(2-pyridyl) disulfide]cobalt(II) are consistent with those reported earlier for this complex.[14–16] The ir spectrum (in a Nujol mull) can be catagorized as belonging to series "II",[14] indicating[17–19] the presence of coordinated pyridyl groups by shifts of the ν(C=C) and ν(C=N) bands generally to higher energy, i.e., of the 1568-, 1552-, 1440-, and 1412-cm^{-1} bands in the free ligand to 1583, 1552, 1450, and 1407 cm^{-1}, respectively, in the complex. This is also indicated by the disappearance of the ring-breathing mode at 980 cm^{-1} in the uncoordinated ligand and its replacement by a 1022–1012-cm^{-1} band in the complex. It has been suggested[14] that the pyridine rings are chemically equivalent but are not related by a symmetry operation and hence that the coordinated ligand in the Co(II) complex probably has a gauche conformation. The crystal structure (see Discussion) confirms this spectral interpretation.

The visible–uv spectra (of Nujol mulls) exhibit strong absorptions at 250, 287, 575, and 606 nm. The first two absorptions are due to the pyridine chromophore and are significantly red-shifted from the corresponding 228- and 272-nm bands in the free ligand. The moderately intense bands at 575 and 606 nm are absorptions typical of tetrahedral complexes.[16]

A very intense Raman band at 522 cm^{-1} is observed for the complex and is assigned to ν(S–S) because it lies within the ν(S–S) region (520–540 cm^{-1}) of diaryl disulfides.[20,21] This band represents a significant shift of 25 cm^{-1} to lower energy relative to that of the uncomplexed ligand. This correlates with the observed increase in the S–S bond length in this complex (see Discussion) as compared to that in the free ligand.

Diffraction Section

A single crystal of $Co(C_{10}H_8N_2S_2)Cl_2$ of extreme dimensions 0.10 × 0.18 × 0.40 mm was selected for x-ray diffraction study and was mounted approximately parallel to its longest dimension.

A Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation (Kα_1, λ 0.70930; Kα_2, λ 0.71359 Å) and with a pulse height analyzer was used for preliminary experiments and for the measurement of diffraction intensities. The cell constants and their standard deviations were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 23°. The program used was written by R. A. Sparks and is part of the diffractometer program library. The temperature was maintained at 24 (2) °C throughout. The θ–2θ scan mode was used with a scan rate (ω) in 2θ of 1° min^{-1}. The total background counting time, equal to the scan time, was spent equally

Table I. Fractional Atomic Coordinates (× 10^4) and Thermal Parameters (× 10^4) for Nonhydrogen Atoms[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	60 (1)	2276 (1)	2011 (1)	106 (2)	57 (1)	194 (2)	28 (1)	92 (1)	33 (1)
Cl(2)	2565 (2)	2296 (1)	4770 (2)	126 (3)	73 (1)	216 (4)	31 (2)	74 (3)	46 (2)
Cl(3)	−178 (2)	1313 (1)	−1038 (2)	164 (3)	78 (1)	199 (4)	43 (2)	102 (3)	25 (2)
N(4)	−2059 (6)	1621 (4)	2421 (7)	114 (10)	57 (4)	187 (12)	31 (5)	87 (9)	30 (6)
C(5)	−1883 (8)	889 (5)	3440 (9)	141 (13)	65 (5)	205 (16)	24 (7)	86 (12)	36 (8)
C(6)	−3350 (9)	323 (5)	3560 (9)	196 (15)	62 (5)	226 (17)	25 (7)	141 (13)	39 (8)
C(7)	−5057 (9)	558 (6)	2629 (10)	183 (15)	71 (6)	244 (18)	2 (8)	155 (14)	14 (9)
C(8)	−5265 (8)	1331 (6)	1608 (9)	112 (12)	71 (6)	221 (16)	24 (7)	94 (12)	13 (8)
C(9)	−3761 (7)	1850 (5)	1518 (8)	107 (11)	62 (5)	161 (14)	21 (6)	71 (11)	11 (7)
S(10)	−3989 (2)	2760 (1)	60 (2)	136 (3)	81 (2)	185 (4)	27 (2)	64 (3)	44 (2)
S(11)	−2780 (2)	4446 (1)	2171 (3)	169 (4)	69 (1)	279 (5)	54 (2)	149 (4)	43 (2)
C(12)	−531 (8)	4841 (5)	2389 (8)	146 (12)	62 (5)	160 (14)	34 (7)	91 (11)	34 (7)
C(13)	68 (9)	6010 (5)	2662 (9)	227 (16)	54 (5)	203 (16)	40 (8)	112 (14)	31 (8)
C(14)	1824 (10)	6391 (5)	2953 (9)	245 (17)	49 (5)	218 (17)	9 (8)	119 (14)	27 (8)
C(15)	2960 (9)	5590 (6)	2926 (9)	181 (14)	70 (6)	223 (17)	8 (8)	109 (13)	39 (8)
C(16)	2256 (8)	4451 (5)	2621 (9)	149 (13)	61 (5)	234 (17)	23 (7)	113 (13)	38 (8)
N(17)	540 (6)	4047 (4)	2371 (7)	119 (10)	53 (4)	185 (12)	27 (5)	85 (9)	30 (6)

[a] See Figure 1 for the identities of the atoms. The estimated standard deviation is in the units of the least significant digit given for the corresponding parameter. The temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

at each end of the scan range, which varied from 2.2° at low 2θ to 2.6° at 55°. The intensities of three check reflections, which were remeasured after every 100 reflections during data collection, showed an average decrease of 3%, for which the appropriate decay correction was applied.

Standard deviations were assigned to the intensities of the individual reflections according to the formula

$$\sigma(I) = [\omega^2(\mathrm{CT} + B_1 + B_2) + (pI)^2]^{1/2}$$

where ω is the scan rate, CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for instrumental inaccuracies. The weights (w) used in least-squares refinement of the structural parameters were the reciprocal squares of $\sigma(F_o)$. Of the 2297 symmetry-independent reflections measured, those for which $2\theta < 55°$, 1898 had intensities larger than 3 times their standard deviations, and only these were used in subsequent calculations. The intensities were corrected[22] for Lorentz and polarization effects. The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction. An absorption correction (μ = 20.66 $\mathrm{cm^{-1}}$) was applied[23] which approximated the crystal shape by a 6 × 6 × 6 grid;[24] the calculated transmission coefficients ranged from 0.77 to 0.89.

The atomic scattering factors for $\mathrm{Co^{2+}}$, $\mathrm{Cl^-}$, $\mathrm{S^0}$, $\mathrm{N^0}$, $\mathrm{C^0}$,[25] and H (bonded)[26] were used. The first three were modified to include the anomalous dispersion correction.[27]

Crystal Data

Dichloro[bis(2-pyridyl) disulfide]cobalt(II), alternatively named dichloro(2,2′-dithiodipyridine)cobalt(II), crystallizes as blue prisms in the triclinic space group $P\bar{1}$: a = 8.132 (4) Å, b = 12.075 (9) Å, c = 7.823 (7) Å, α = 107.30 (6)°, β = 114.85 (5)°, γ = 94.47 (5)°, V = 647.1 (8) $\mathrm{Å^3}$, mol wt 350.2, d_{obsd}(flotation) = 1.79 (1) g $\mathrm{cm^{-3}}$, d_{calcd} = 1.797 (2) g $\mathrm{cm^{-3}}$, Z = 2, and $F(000)$ = 350. Figures in parentheses are estimated standard deviations in the units of the least significant digit given for the corresponding parameter.

Structure Determination

The position of Co(II) was indicated on a three-dimensional Patterson function which was prepared using the fast-Fourier algorithm.[28] The positions of all other nonhydrogen atoms were found by successive cycles of Fourier refinement. Hydrogen atom positions were calculated[29] assuming the C–H distance to be 0.95 Å.[30] Full-matrix least-squares refinement[31] with anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters (initially equal to those of the attached carbon atoms) for hydrogen atoms led to the final error indices $R_1 = \sum|F_o - |F_c||/\sum F_o = 0.050$ and $R_2 = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.059$. The "goodness-of-fit", $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 3.50, somewhat large, in part because of the difficulties encountered in applying the absorption correction accurately to the irregular crystal used. (However, this correction is still somewhat better than none at all—refinements using data uncorrected for absorption converged with R_1 = 0.052 and R_2 = 0.061.) The number of observations used in least squares is m (1898), and s (186) is the total number of parameters. The overdetermination ratio (m/s) is 10.2. In the final cycles of least-squares all shifts in atomic and thermal parameters for nonhydrogen atoms were less than 1% of their esd's. For the hydrogen atoms the largest shift in a positional parameter was 5% of its esd, and for a thermal parameter, 12%. The largest peak on the final difference Fourier function, whose esd is 0.16 e $\mathrm{Å^{-3}}$, was 1.0 e $\mathrm{Å^{-3}}$ in height and was located very near the Co(II) ion at a chemically implausible position. The positional and thermal parameters of the atoms are given in Tables I and II.

Table II. Fractional Atomic Coordinates (× 10^3) and Thermal Parameters ($\mathrm{Å^2}$) for Hydrogen Atoms[a]

Atom	x	y	z	B
H(5)	−71 (8)	88 (5)	414 (9)	4.9 (1.4)
H(6)	−311 (7)	−15 (4)	434 (7)	2.6 (1.1)
H(7)	−606 (8)	15 (5)	248 (8)	3.9 (1.3)
H(8)	−638 (7)	148 (5)	92 (8)	3.7 (1.2)
H(13)	−79 (7)	652 (5)	268 (8)	3.3 (1.2)
H(14)	219 (8)	717 (5)	325 (8)	3.9 (1.3)
H(15)	413 (9)	579 (6)	313 (10)	6.7 (1.8)
H(16)	299 (8)	387 (5)	261 (8)	4.1 (1.3)

[a] See Figure 1 for the identities of the atoms. The esd is in the units of the least significant digit given for the corresponding parameter.

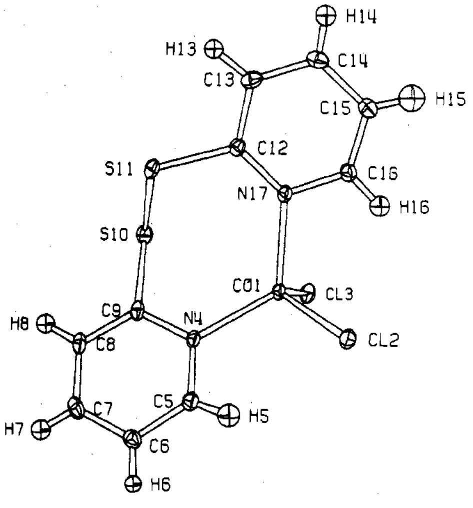

Figure 1. Molecular structure of $\mathrm{Co(C_{10}H_8N_2S_2)Cl_2}$. Ellipsoids of 15% probability are used.[32]

Discussion

The structure consists of neutral molecules of composition $\mathrm{Co(C_{10}H_8N_2S_2)Cl_2}$ (see Figures 1 and 2). The tetrahedral Co(II) ion is coordinated by two chloride ions and by the two pyridyl nitrogen atoms of a single bis(2-pyridyl) disulfide

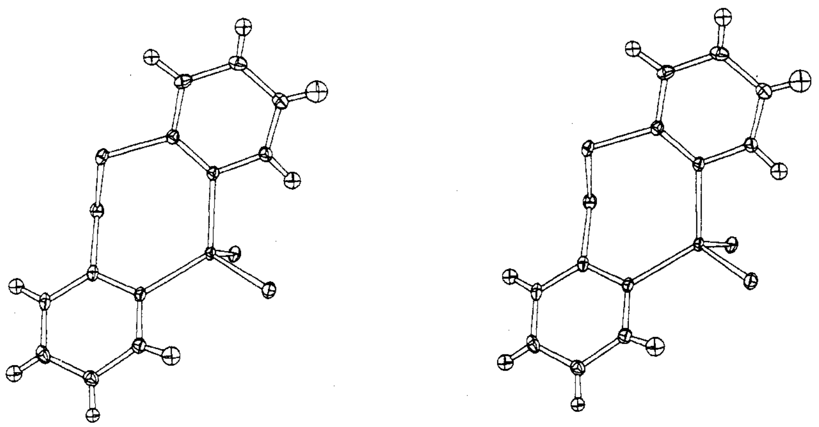

Figure 2. Stereoview of $Co(C_{10}H_8N_2S_2)Cl_2$ showing ellipsoids of 15% probability.[32]

ligand, to give a seven-membered $\overline{\text{SCNCoNCS}}$ chelate ring. The disulfide group does not participate in coordination. The angles at Co(II) range from 101 to 118°, as is shown in Table III, the largest being N–Co–N and Cl–Co–Cl.

The S–S bond length, 2.040 (2) Å, is somewhat longer than that found in the structure of the free ligand, 2.016 (2) Å.[13] This cannot be ascribed to the small deviation of the C–S–S–C torsion angle (102.2°) from 90°,[33] nor is it a direct effect of the coordination of the disulfide group to the metal ion,[7,8] because such coordination is absent in this complex.

Furthermore, a discussion of π interactions between the disulfide group and the aromatic rings does not lead to an entirely satisfactory explanation[13] for the change in S–S bond length upon complexation. Complexation to $CoCl_2$ has caused the disulfide group to rotate relatively far from the plane of either pyridine ring (see the deviations of S(11) from plane 1 and of S(10) from plane 2 in Table IV), unlike the situation in the structure of the uncomplexed ligand[13] where near planarity is observed. This suggests that a π interaction between the aromatic ring and the disulfide group has been disrupted, lengthening the S–S bond. However, some organic disulfides have S–S bonds as short as those of free bis(2-pyridyl) disulfide even though their sulfur atoms are bonded to saturated carbons, with which a π interaction cannot occur.[34,35]

It remains possible that the inductive (σ) effect of Co(II) coordinated to nitrogen is partially responsible for the lengthening S–S bond. Also, as has been noted in the Cu(I) complex[9] of this same ligand, the S–S bonds are longer when the C–C–S–S torsion angles involving unsaturated systems bonded to sulfur deviate widely from 0° (or 180°) as they have in this complex.

The Co(II)–N coordination distances average 2.040 Å. This is in agreement with the equivalent average found in dichlorobis(3-methylpyridine)cobalt(II),[36] 2.05 (1) Å, and in dichlorobis(4-vinylpyridine)cobalt(II),[37] 2.01 (2) Å. In an analogous imidazole complex of $CoCl_2$, an average distance of 1.99 (1) Å was found.[38]

The N–Co(II)–N angle, 117.9 (2)°, is appreciably larger than those of 107 (1),[36] 107 (2),[37] and 105.4 (5)°[38] observed in the structures named in the preceding paragraph. Presumably this is a consequence of the steric requirements of the seven-membered chelate ring.

The Co(II)–Cl distances average 2.246 Å, in agreement with 2.23 (1) Å in dichlorobis(3-methylpyridine)cobalt(II),[36] 2.22 (1) Å in dichlorobis(4-vinylpyridine)cobalt(II),[37] 2.237 (5) and 2.264 (4) Å in dichlorobis(imidazole)cobalt(II),[38] and 2.229 (3) Å in dichloro(ethylenedimorpholine)cobalt(II),[39] whose nitrogen ligands are saturated.

The Cl–Co(II)–Cl angle, 118.5 (1)°, compares with those of 121 (1),[36] 117 (1),[37] 111.2 (2),[38] and 116.8 (2)°,[39] all greater than the tetrahedral angle, which occurred in the structures named in the previous paragraph.

Table III. Molecular Dimensions and Esd's[a]

A. Bond Lengths, Å

Co(1)–Cl(2)	2.253 (2)	C(12)–C(13)	1.379 (8)
Co(1)–Cl(3)	2.238 (2)	C(13)–C(14)	1.366 (9)
Co(1)–N(4)	2.025 (4)	C(14)–C(15)	1.391 (9)
Co(1)–N(17)	2.055 (4)	C(15)–C(16)	1.358 (9)
S(10)–S(11)	2.040 (2)	C(5)–H(5)	0.88 (6)
S(10)–C(9)	1.773 (6)	C(6)–H(6)	0.93 (5)
S(11)–C(12)	1.776 (6)	C(7)–H(7)	0.86 (6)
N(4)–C(5)	1.334 (7)	C(8)–H(8)	0.90 (5)
N(4)–C(9)	1.358 (7)	C(13)–H(13)	0.96 (5)
N(17)–C(12)	1.345 (7)	C(14)–H(14)	0.89 (6)
N(17)–C(16)	1.353 (7)	C(15)–H(15)	0.89 (7)
C(5)–C(6)	1.380 (8)	C(16)–H(16)	0.96 (5)
C(6)–C(7)	1.368 (9)		
C(7)–C(8)	1.376 (9)		
C(8)–C(9)	1.369 (8)		

B. Bond Angles, Deg

Cl(2)–Co(1)–Cl(3)	118.5 (1)	N(17)–C(12)–C(13)	122.6 (5)
Cl(2)–Co(1)–N(4)	101.6 (1)	C(12)–C(13)–C(14)	119.2 (6)
Cl(2)–Co(1)–N(17)	100.7 (1)	C(13)–C(14)–C(15)	119.6 (6)
Cl(3)–Co(1)–N(4)	113.8 (1)	C(14)–C(15)–C(16)	117.5 (6)
Cl(3)–Co(1)–N(17)	104.3 (1)	C(15)–C(16)–N(17)	124.6 (6)
N(4)–Co(1)–N(17)	117.9 (2)	C(16)–N(17)–C(12)	116.4 (5)
Co(1)–N(4)–C(5)	121.9 (4)	H(5)–C(5)–N(4)	112 (4)
Co(1)–N(4)–C(9)	119.9 (4)	H(5)–C(5)–C(6)	124 (4)
Co(1)–N(17)–C(12)	131.8 (4)	H(6)–C(6)–C(5)	118 (3)
Co(1)–N(17)–C(16)	111.8 (4)	H(6)–C(6)–C(7)	124 (3)
S(10)–S(11)–C(12)	106.8 (2)	H(7)–C(7)–C(6)	122 (4)
S(11)–S(10)–C(9)	103.9 (2)	H(7)–C(7)–C(8)	117 (4)
S(10)–C(9)–N(4)	117.1 (4)	H(8)–C(8)–C(7)	123 (3)
S(10)–C(9)–C(8)	121.4 (4)	H(8)–C(8)–C(9)	118 (3)
S(11)–C(12)–N(17)	121.2 (4)	H(13)–C(13)–C(12)	117 (3)
S(11)–C(12)–C(13)	116.1 (4)	H(13)–C(13)–C(14)	124 (3)
N(4)–C(5)–C(6)	123.4 (6)	H(14)–C(14)–C(13)	116 (4)
C(5)–C(6)–C(7)	117.8 (6)	H(14)–C(14)–C(15)	124 (4)
C(6)–C(7)–C(8)	119.9 (6)	H(15)–C(15)–C(14)	123 (4)
C(7)–C(8)–C(9)	119.5 (5)	H(15)–C(15)–C(16)	119 (4)
C(8)–C(9)–N(4)	121.4 (5)	H(16)–C(16)–C(15)	121 (3)
C(9)–N(4)–C(5)	118.0 (5)	H(16)–C(16)–N(17)	115 (3)

C. Selected Torsion Angles, Deg

C(9)–S(10)–S(11)–C(12)	102.2
C(8)–C(9)–S(10)–S(11)	107.2
C(13)–C(12)–S(11)–S(10)	142.3
N(4)–C(9)–S(10)–S(11)	77.4
N(17)–C(12)–S(11)–S(10)	40.4
Co(1)–N(4)–C(9)–S(10)	1.5
Co(1)–N(17)–C(12)–S(11)	2.8
N(4)–Co(1)–N(17)–C(12)	17.7

[a] The esd is in the units of the least significant digit given for the corresponding parameter.

Table IV. Deviations of Atoms from Least-Squares Planes (Å × 10^3)[a]

	Plane 1		Plane 2		Plane 3		Plane 4	
	N(4)	*−8*	N(17)	*5*	N(4)	*0*	Cl(2)	*0*
	C(5)	*13*	C(12)	*0*	Co(1)	*0*	Co(1)	*0*
	C(6)	*−6*	C(13)	*−7*	N(17)	*0*	Cl(3)	*0*
	C(7)	*−6*	C(14)	*8*	C(9)	−873	N(4)	−1616
	C(8)	*5*	C(15)	*2*	S(10)	−1947	S(10)	−355
	C(9)	*2*	C(16)	*−8*	S(11)	−750	S(11)	1079
	Co(1)	−199	Co(1)	20	C(12)	−304	N(17)	1861
	S(10)	−117	S(10)	−1113				
	S(11)	1760	S(11)	79				
	Cl(2)	722	N(4)	572				
	N(17)	992						
$q_{b\times(a\times b)}$	−1896		−1088		1978		5339	
q_b	5150		−1098		−1397		8443	
$q_{a\times b}$	8359		9881		9702		460	
D	2.606		1.116		0.843		1.636	
δ	7		6		0		0	

[a] Italic deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with coordinates given in Table I lies between that plane and the origin. The direction cosines (× 10^4), q, are with respect to orthogonalized axes. The rms deviation (Å × 10^3) of the atoms defining the plane from the plane is δ. D is the distance (in Å) from the plane to the origin. See Figure 1 to identify the planes.

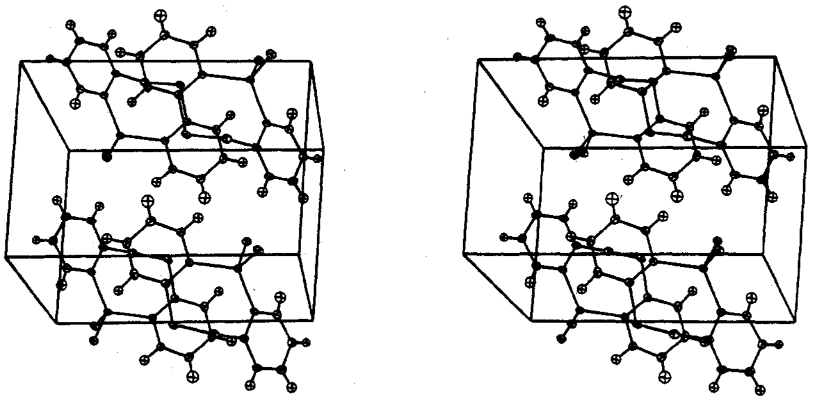

Figure 3. Stereoview of the structure, illustrating the packing of molecules within the unit cell. Ellipsoids of 15% probability are used.[32] The view is approximately into a with b horizontal and c nearly vertical in the plane of the page.

Dichloro[bis(2-pyridyl) disulfide]cobalt(II) does not have molecular symmetry, nor is it close to having any, as can be seen in the geometry presented in Tables III and IV and in Figure 2.

Altogether, the following changes have occurred in the geometry of bis(2-pyridyl) disulfide[13] upon its coordination to $CoCl_2$ through its pyridyl nitrogen atoms. The S–S bond has increased in length from 2.016 (2) to 2.040 (2) Å. The C–S distance has decreased from 1.785 (2) to 1.774 (4) Å. The C–S–S–C torsion angle has increased from 87.1 to 102.2°. The S–S–C–C torsion angles have increased from 2.7 and 10.2 to 107.2 and 142.3°. The C–N bond has increased from 1.328 (3) Å, the average value in the ordered ring in the structure of the free ligand, to 1.348 (4) Å upon N coordination. The 12° discrepancy between the internal and external S–C–(C or N) angles (see Figure 1 and Table IIIB) has disappeared upon coordination; this is related to the rotation of the S–S bond out of the plane of each of the pyridine rings upon coordination.

The molecular packing is shown in Figure 3 and does not indicate any unusually close intermolecular contacts. The shortest intermolecular distances not involving hydrogen are Cl(2)–C(7) = 3.50 Å, C(7)–C(9) = 3.35 Å, C(7)–C(8) = 3.55 Å, C(6)–C(8) = 3.55 Å, and C(13)–C(16) = 3.59 Å.

Acknowledgment. This work was supported by the National Institutes of Health (Grant No. GM-18813-04). We are also indebted to the University of Hawaii Computing Center.

Registry No. $Co(C_{10}H_8N_2S_2)Cl_2$, 31233-09-7.

Supplementary Material Available: Listing of structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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Molecular Structure and Spectral Properties of Phosphatriazaadamantanemolybdenum Pentacarbonyl Complex

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Received December 1, 1975 AIC50857Z

The crystal and molecular structure of $Mo(CO)_5[P(CH_2)_6N_3]$ has been determined by single-crystal x-ray diffraction techniques using a GE 490 automated diffractometer system. The compound crystallizes in the space group *Pbca* with eight formula weights in a unit cell of dimensions $a = 14.357$ (2) Å, $b = 26.509$ (2) Å, and $c = 8.1528$ (6) Å. The structure was solved by means of a three-dimensional Patterson function and refined by block-diagonal least squares to a value of $R = 0.069$ for 1194 statistically significant reflections. The ligand has been shown to bind to the molybdenum through the phosphorus with a Mo–P bond of 2.48 Å. The rigidity of the phosphorus cage which exists both in the solid and in solution allows for a crystallographic estimate of Tolman's widely used steric factor, the "ligand cone angle". Infrared spectral properties are compared to metal carbonyl derivatives of other phosphorus cage compounds.

Introduction

A novel phosphatriazaadamantane, PTA (Figure 1), and its analogues have recently been reported[1] in the literature. This tetrabasic nonchelating cage compound readily forms complexes with low-valent metal carbonyls in which the ligand is apparently phosphorus bound.[2] Multicomplexation of the ligand has been observed in the preparation of $[W(CO)_5PTA]_2Hg_2Cl_4$.[3] Since the detailed geometry of this cage system is unknown, and in light of the recent interest in phosphorus-containing cage molecules,[4-8] the molecular structure of a PTA derivative, $Mo(CO)_5PTA$, was determined and is the subject of this report.

Experimental Section

$Mo(CO)_5PTA$ was prepared[2] and recrystallized from boiling hexane. Tetraphosphorus trisulfide was recrystallized from benzene and over a period of days at room temperature displaced piperidine from $Mo(CO)_5(NHC_6H_{11})$ in hexane solution yielding $Mo(CO)_5P_4S_3$ as identified by its principal ν_{CO} bands in the infrared spectrum.[4] Infrared spectra were taken on a Perkin-Elmer 521 spectrophotometer.

X-Ray Data. A platelike crystal of the molybdenum complex approximately 0.25 mm long on the face side and with a thickness of 0.10 mm was mounted on a General Electric XRD-5 diffractometer with the (001) axis as the spindle axis. Extinctions for the reflections with $h = 2n + 1$ in the (hk0) data, those with $l = 2n + 1$ in the ($h0l$) data, and those with $k = 2n + 1$ in the (0kl) data combined with *mmm* symmetry in reciprocal space uniquely characterize the orthorhombic space group *Pbca*. Lattice constants were determined by a least-squares fit of 15 carefully measured 2θ values (1° TOA and 0.05° slit) at $2\theta > 70°$ where the Cu $K\alpha_1$, $K\alpha_2$ doublet is easily resolved.

The resultant lattice constants and their estimated standard deviations are $a = 14.357 \pm 0.002$ Å, $b = 26.509 \pm 0.002$ Å, and $c = 8.1528 \pm 0.0006$ Å.

The calculated density of 1.68 g/cm^3 for eight molecules per unit cell agrees with an experimentally measured (using flotation techniques) density of 1.71 (2) g/cm^3.

A set of three-dimensional intensity data were collected on a General Electric XRD-490 fully automated diffractometer by the stationary-counter, stationary-crystal method. Balanced nickel–cobalt filters with copper $K\alpha$ radiation were used to measure all reflections out to a 2θ maximum of 100°. A total of 1887 independent reflections were measured with 1194 considered as statistically significant based on the criterion

$$(I_{Ni} - 2\sigma(I_{Ni})) - (I_{Co} + 2\sigma(I_{Co})) > 100$$

where the σ's were based solely on counting statistics for the 10-s count. The intensities were corrected for α_1–α_2 splitting as a function of 2θ and for absorption as a function of ϕ (linear $\mu = 84.5$ cm^{-1} with a ratio of 1.18:1 in the absorption correction). Lorentz–polarization corrections were made and the intensities reduced to structure amplitudes in the usual manner.

Structure Determination. The three-dimensional Patterson function clearly indicated the Mo–Mo, Mo–P interactions although there was an ambiguity with respect to the P–P interactions. A Fourier map based only on the Mo position ($R = 0.42$)[5] and another based on the Mo, P positions ($R = 0.34$) gave similar results. The adamantane-like structure was easily deciphered although the anisotropy of the Mo partially masked the locations of the carbonyl groups. A series of least-squares cycles was run using the Mo, P and adamantane ring (11 atoms). This refinement lowered the value of the residual index to $R = 0.26$ and a Fourier map was calculated at this point. Four of the five carbonyl groups were readily evident, with the carbon of the fifth group still partially obscured by the Mo peak. Another cycle involving least-squares and Fourier refinement led to the location of the fifth carbonyl group. The Mo was assigned anisotropic temperature factors, the remaining atoms retaining isotropic temperature factors, and ten cycles of least-squares refinement resulted in a value of $R = 0.145$. All of the 21 atoms were then converted to anisotropic temperature factors and ten additional cycles of block-diagonal

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