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Crystal and Molecular Structure of the Macrocyclic Nickel(II) Complex $Ni(C_{18}H_{14}N_4)$: Dibenzo[*b,i*][1,4,8,11]tetraaza[14]annulenenickel(II)

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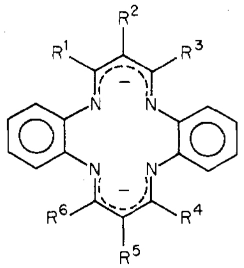
The crystal and molecular structure of the four-coordinate complex $Ni(C_{18}H_{14}N_4)$ containing the dibenzotetraaza[14]annulene ligand has been determined from three-dimensional x-ray diffraction data. The complex crystallizes in the monoclinic space group C_{2h}^5-$P2_1/c$ with cell dimensions $a = 19.456$ (4) Å, $b = 5.228$ (1) Å, $c = 14.868$ (3) Å, and $\beta = 112.28$ (1)° with $Z = 4$, the unit cell containing two independent molecules each lying on a crystallographic inversion center. The cobalt(II) complex $Co(C_{18}H_{14}N_4)$ is isostructural with cell dimensions $a = 19.52$ (1) Å, $b = 5.228$ (1) Å, $c = 14.84$ (1) Å, and $\beta = 112.46°$. The nickel structure was refined by Fourier and least-squares techniques to a conventional R value of 4.1% based on 3112 reflections with $F > 3\sigma_F$. The average Ni–N distance is 1.870 Å. Although the macrocyclic ring is essentially planar in each molecule, the delocalized propane-1,3-diiminato chelate rings and the benzenoid rings are linked by nominally single C–N bonds.

Introduction

The chemistry associated with highly conjugated and completely conjugated macrocyclic complexes is considerably different from that of their saturated counterparts. Highly delocalized conjugated ligand systems interact strongly with coordinated metals and greatly influence the physical and chemical properties of the metal.[1] With very flat macrocyclic ligands intermolecular interactions may occur.[2] Both solid-state and solution intermolecular interactions have been documented.[3]

A large number of macrocyclic complexes have been synthesized and characterized which are based on the dibenzotetraaza[14]annulene framework[4-6]



Crystallographic studies have shown that when R^1, R^3, R^4, R^6 = CH_3 strong intramolecular steric interactions of the methyl groups with the benzenoid rings cause marked deviation from ligand planarity leading to a pronounced saddle-shaped ligand.[7] These peripheral steric constraints are responsible for unusual and unique chemical reactivity observed in the metal complexes of this ligand.[8]

The crystal and molecular structure of the title compound, prototypic of the dibenzotetraaza[14]annulenes, was undertaken to extend and elucidate structural tendencies parameterized by the crystallographic characterization of the various substituted analogues. Also it was important to determine if the extent of π delocalization throughout the 14-membered inner ring of the macrocyclic ligand, as inferred from bond distances, is a detectable function of the departure from ligand planarity.

Experimental Section

A sample of the title compound was prepared according to the method of Dolphin.[9] Crystals suitable for x-ray diffraction studies were grown by slow vacuum sublimation in a sealed tube. A well-formed crystal, 0.5 × 0.15 × 0.10 mm, was selected. Zero-level precession and Weissenberg photographs had systematic absences indicating orthorhombic space groups *Fdd*2 or *Fddd*. However, examination of the upper-level photographs clearly indicated monoclinic symmetry with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, establishing C_{2h}^5-$P2_1/c$ as the unique space group.

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Table I. Crystal Data for $M(C_{18}H_{14}N_4)$; M = Ni(II), Co(II)

	$Ni(C_{18}H_{14}N_4)$	$Co(C_{18}H_{14}N_4)$
Mol wt	345.07	345.29
Space group	$P2_1/c$	$P2_1/c$
Cell constants		
a, Å	19.456 (4)	19.52 (1)
b, Å	5.228 (1)	5.228 (4)
c, Å	14.868 (3)	14.84 (1)
α, deg	90.0	90.0
β, deg	112.28 (1)	112.46 (3)
γ, deg	90.0	90.0
No. of reflections used to determine cell constants and their 2θ limits, deg	30; $40 < 2\theta < 50$	29; $30 < 2\theta < 50$
Z	4	4
ρ_{calcd}, g/cm³	1.638	1.639
ρ_{exptl}, g/cm³	1.64	1.64
μ, cm⁻¹	13.89	12.78

Table II. Data Collection and Refinement Details for $Ni(C_{18}H_{14}N_4)$

Diffractometer	Picker FACS-1
Monochromator (Bragg angle)	Graphite (6.093 Å)
Radiation	Mo Kα (λ 0.710 69 Å)
Takeoff angle	3°
Method	θ–2θ
Scan speed	2°/min
Scan width[a]	2°
Background	20 × 2 s
Standards	3
Max dev of standards	3%
2θ limits of data	$0° < 2\theta < 70°$
No. of data collected	4744
No. of data in final refinement	3112 ($F > 3\sigma_F$)
R_1[b]	4.1%
R_2[c]	4.0%

[a] Scan width at 0 °C; a symmetrical dispersion factor of 0.692 was used to account for α_1–α_2 splitting at increasing values of 2θ. [b] $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [c] $R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w \cdot (F_o)^2]^{1/2}$.

Other zero-level absences were a consequence of orthorhombic pseudosymmetry. The cobalt(II) analogue was prepared by a similar method, and crystals were grown by vacuum sublimation. X-ray powder diffraction patterns, preliminary precession photographs, and cell dimensions indicate that the cobalt(II) structure and the nickel(II) structure are isostructural. Crystal data and data collection details are tabulated in Tables I and II.[10] A symmetrical dispersion factor of 0.692 was used to account for α_1–α_2 splitting at increasing 2θ values. During the course of the data collection, three standard reflections well distributed in reciprocal space were measured every 100 reflections to monitor crystal quality and alignment.

Relative intensities and their standard deviations were calculated by $I = S - tB$ and $\sigma_I = [S + t^2B + k^2(S + tB)^2]^{1/2}$ where *S* is the peak scan counts, *B* is the total background scan counts, *t* is the ratio of peak to background scan times, and *k* is an instability constant here taken as 0.02 to account for machine fluctuations and other sources of error influencing the diffracted intensity.[11] The observed structure factors and their standard deviations were calculated by $F_o = (I/Lp)^{1/2}$ and $\sigma_{F_o} = [(I + \sigma_I)/Lp]^{1/2} - [I/Lp]^{1/2}$ where *Lp* is the Lorentz–polarization factor.

Solution and Refinement of the Structure

Normalized structure factors were calculated by Wilson's method and an analysis of the data indicated a centrosymmetric structure. The phase problem was solved by MULTAN[12] by the tangent formula method. Of the 16 solutions generated, that of the highest figure of merit (FOM = 0.9412) and lowest residual (*R* = 0.25) yielded an *E* map revealing two molecular fragments each containing 12 atoms. These fragments corresponded to the carbon–nitrogen frameworks of two independent molecules with their nickel atoms located at inversion centers $^1/_2$, 0, $^1/_2$ and 0, $^1/_2$, 0. The nickel atoms, however, were not found on the *E* map. Two cycles of full-matrix least-squares refinement with anisotropic thermal parameters for the nickel atoms and isotropic thermal parameters for all other nonhydrogen atoms reduced the conventional and weighted *R* values to 4.5% and 5.6%, respectively. A difference Fourier map revealed the positions of all hydrogen atoms. Contributions from these atoms in fixed, idealized positions (assuming sp² geometry and with C–H distances of 0.95 Å) and *B* values of 3.5 Å² were included in the final least-squares calculations. The final two least-squares cycles varied positional and anisotropic thermal parameters of all nonhydrogen atoms. At convergence the conventional unweighted and weighted *R* values were 0.041 and 0.040 for 3112 observed structure factors with $R > 3\sigma_F$, with the standard deviation of an observation of unit weight being 1.79. The number of varied parameters was 211 with a data to parameter ratio of 14.75. Examination of the final difference Fourier map revealed a maximum residual electron density of 0.70 e/Å³ near one of the nickel atoms. The final positional and thermal parameters are listed in Tables III–V.

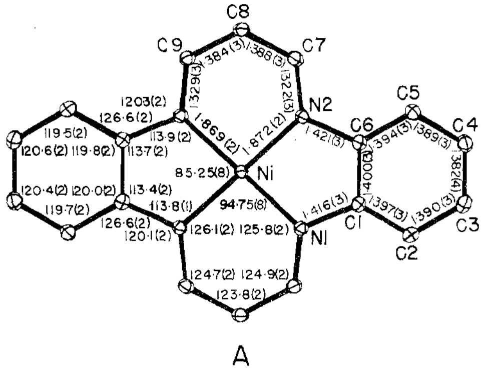

Figure 1. ORTEP plot of $Ni(C_{18}H_{14}N_4)$ molecule A with a labeling diagram and selected interatomic distances and angles. The thermal ellipsoids are drawn to the 20% probability level. The number in parentheses following each datum is the estimated standard deviation in the last significant figure.

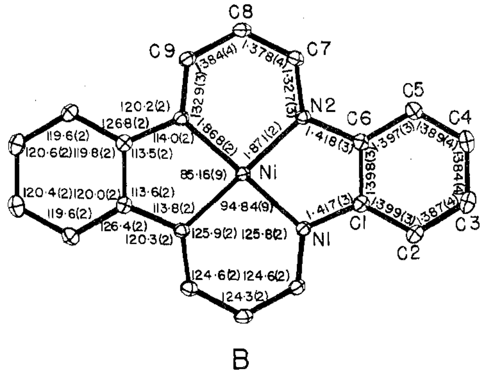

Figure 2. ORTEP plot of $Ni(C_{18}H_{14}N_4)$ molecule B. Pertinent data are given in the caption to Figure 1.

A listing of the observed and calculated structure factors is given as supplementary material (see paragraph at the end of paper).

Description and Discussion of the Structure

The crystal structure of the title compound reveals two independent molecules of the four-coordinate square-planar complex $Ni(C_{18}H_{14}N_4)$ with each molecule positioned on a crystallographic inversion center. Figures 1 and 2 are drawings of the two independent molecules with a labeling scheme and selected interatomic distances and angles. In the two molecules all chemically equivalent bond distances and angles are essentially identical. The macrocyclic complex is planar; the maximum deviation of any atom from the least-squares plane of each molecule is 0.04 Å (Figure 3).

The macrocyclic complex contains delocalized six-membered propane-1,3-diiminato chelate rings which are separated from the aromatic benzenoid rings by nominally single C–N bonds, the average bond length being 1.418 Å. The interatomic distances within each of the benzenoid rings are very close to the accepted aromatic distance of 1.398 Å. Perhaps the most

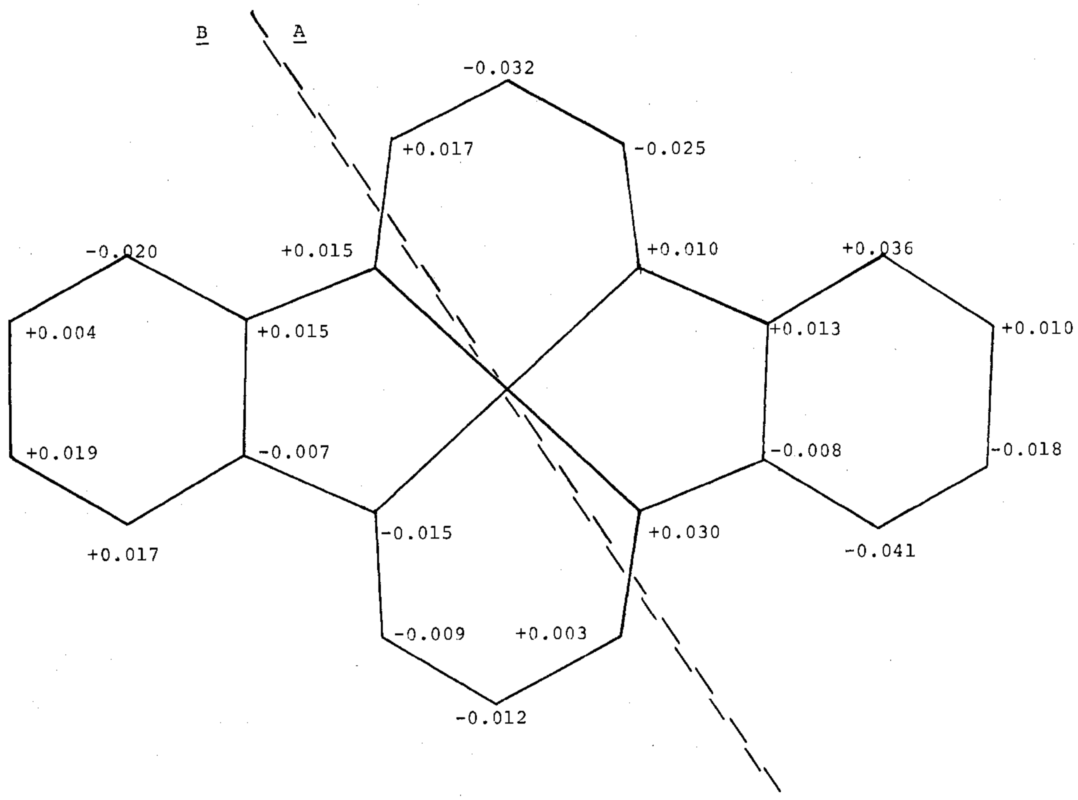

Figure 3. Diagrammatic representation illustrating the deviation of the individual atoms of the macrocyclic ligand from the least-squares plane of the ligand for molecules A and B.

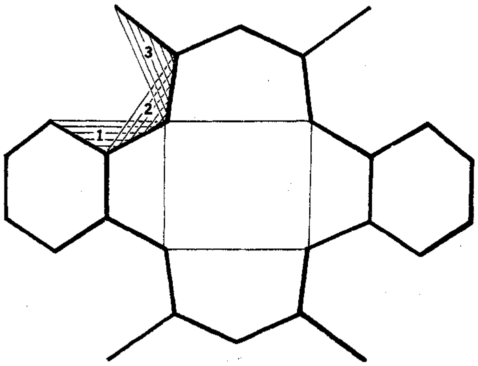

Figure 4. Planes defining the dihedral twist angles in $M(C_{22}H_{22}N_4)L_m$ (m = 0, 1, 2), the metal complexes of the tetramethyldibenzotetraaza[14]annulene ligand. The angle between planes 1 and 2 is the dihedral twist angle about the C–N bond of the five-membered chelate ring; the angle between planes 2 and 3 is the dihedral twist angle about the C–N bond of the six-membered chelate ring.

important bonding feature is the C–N distance in the five-membered chelate ring. While structures of the tetramethylated derivatives have similar bond distances,[7] there was no direct confirmation that the large single-bond character was not a result of the dihedral twist about the C–N bonds of the five-membered chelate ring (Figure 4). The magnitude of the twist varies from 25 to over 50° in the derivatives structurally examined and is a major component for the relief of the steric strain caused by the interaction of the methyl groups with the benzenoid rings. The resultant saddle deformation is a consequence of this and other compensatory features. Observation of an almost identical C–N bond distance in the five-membered rings of the planar dibenzotetraaza[14]annulenenickel(II) species establishes that there is little or no preference for π delocalization between the propane-1,3-diiminato chelate rings and the aromatic benzenoid moieties.

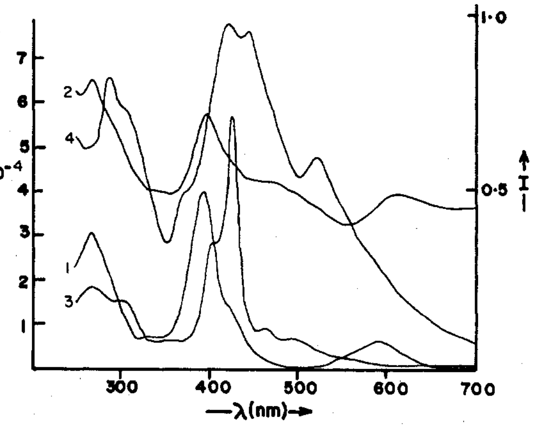

Figure 5. Solution ($CHCl_3$) and solid-state (Nujol mull) spectra for $Ni(C_{18}H_{14}N_4)$ and its tetramethylated derivative $Ni(C_{22}H_{22}N_4)$: $Ni(C_{18}H_{14}N_4)$ solution (1) and solid-state (2) spectra; $Ni(C_{22}H_{22}N_4)$ solution (3) and solid-state (4) spectra. Solid-state spectra are drawn on an arbitrary intensity scale.

The Ni–N distances have an average value of 1.870 Å, which is appreciably shorter than the Ni–N distances observed in a number of porphyrin structures but comparable to those observed in $Ni(dmg)_2$.[13] With respect to other 14-membered ring systems, the Ni–N distances in the title compound are considerably shorter than that recorded for saturated, macrocyclic low-spin nickel(II) complexes which have bond distances in the range 1.95–2.00 Å.[14] Since Ni–N distances as short as 1.78 Å have been observed in a dihydrooctaaza[14]annulene complex of nickel(II),[15] there probably is little compressional strain in the coordination sphere of the dibenzotetraaza[14]annulenenickel(II) complex.

The interatomic distances within the macrocycle are almost invariant between the title complex and the nine structures of its tetramethylated derivative which have been studied.[7] The most significant anomaly in the derivatives, which can be

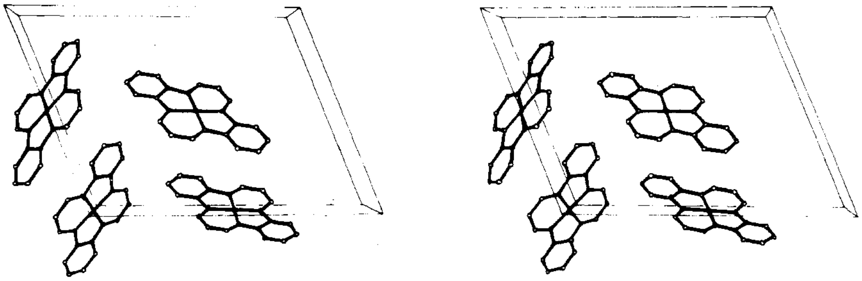

Figure 6. Stereodiagram of the unit cell contents of Ni($C_{18}H_{14}N_4$), viewed down the *b* axis, illustrating the arrangement of the molecules in the unit cell.

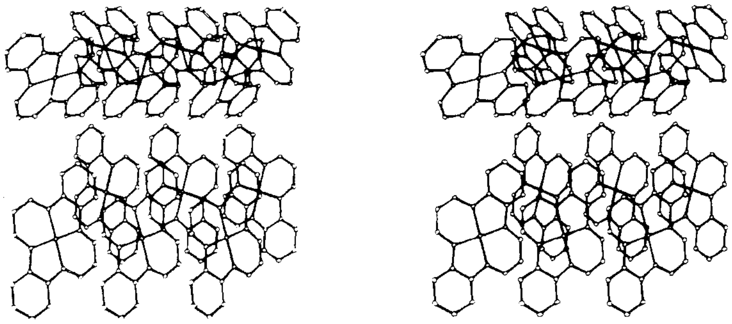

Figure 7. Stereodiagram of Ni($C_{18}H_{14}N_4$), viewed perpendicular to the *ab* face, showing the molecular stacking.

Table III. Final Atomic Positions for Ni($C_{18}H_{14}N_4$)[a]

Atom	*x*	*y*	*z*
A-Ni	0.0000	1.0000	0.5000
A-N1	−0.0920 (1)	1.0840 (4)	0.4043 (1)
A-N2	0.0030 (1)	0.7432 (4)	0.4139 (1)
A-C1	−0.1127 (1)	0.9274 (5)	0.3205 (2)
A-C2	−0.1778 (1)	0.9471 (5)	0.2373 (2)
A-C3	−0.1914 (1)	0.7710 (5)	0.1625 (2)
A-C4	−0.1408 (1)	0.5793 (6)	0.1691 (2)
A-C5	−0.0755 (1)	0.5599 (5)	0.2509 (2)
A-C6	−0.0611 (1)	0.7351 (4)	0.3265 (2)
A-C7	0.0579 (1)	0.5791 (5)	0.4280 (2)
A-C8	0.1228 (1)	0.5712 (5)	0.5106 (2)
A-C9	0.1374 (1)	0.7329 (5)	0.5894 (2)
B-Ni	0.5000	1.0000	0.5000
B-N1	0.4072 (1)	0.9139 (4)	0.5012 (1)
B-N2	0.4989 (1)	0.7456 (4)	0.4110 (1)
B-C1	0.3847 (1)	1.0696 (5)	0.5632 (2)
B-C2	0.6817 (1)	0.9495 (5)	0.4212 (2)
B-C3	0.6962 (1)	0.7775 (6)	0.3596 (2)
B-C4	0.6453 (2)	0.5889 (6)	0.3128 (2)
B-C5	0.5790 (2)	0.5687 (5)	0.3272 (2)
B-C6	0.5637 (1)	0.7408 (5)	0.3890 (2)
B-C7	0.4450 (1)	0.5766 (5)	0.3709 (2)
B-C8	0.3802 (1)	0.5653 (5)	0.3878 (2)
B-C9	0.3634 (1)	0.7266 (5)	0.4505 (2)

[a] The number in parentheses following each datum is the estimated standard deviation in the last significant figure.

Table IV. Hydrogen Atom Positions for Ni($C_{18}H_{14}N_4$)[a]

Atom	On atom	*x*	*y*	*z*
A-H1	A-C2	−0.2138	1.0844	0.2320
A-H2	A-C3	−0.2359	0.7860	0.1054
A-H3	A-C4	−0.1515	0.4574	0.1166
A-H4	A-C5	−0.0398	0.4263	0.2559
A-H5	A-C7	0.0520	0.4554	0.3776
A-H6	A-C8	0.1606	0.4481	0.5129
A-H7	A-C9	0.1838	0.7102	0.6443
B-H1	B-C2	0.7177	1.0810	0.4539
B-H2	B-C3	0.7418	0.7917	0.3484
B-H3	B-C4	0.6565	0.4701	0.2700
B-H4	B-C5	0.5436	0.4357	0.2944
B-H5	B-C7	0.4522	0.4525	0.3272
B-H6	B-C8	0.3434	0.4387	0.3533
B-H7	B-C9	0.3164	0.7027	0.4574

[a] $B = 3.5$ Å^2.

attributed to the compressional and steric effects of the methyl groups, is a lengthening of the C–C bonds of the benzenoid rings fused to the 14-membered core to an average value of 1.420 Å and a shortening on the opposite side of the benzenoid ring to an average value of 1.370 Å.

The solution and solid-state electronic spectra of the title compound and its tetramethylated derivative are presented in Figure 5. As a result of the saddle-shape deformation of Ni($C_{22}H_{22}N_4$), its solution spectrum differs markedly from that of the planar Ni($C_{18}H_{14}N_4$). The differences arise primarily because of the following interdependent reasons: (1) changes in the energy levels of the π systems of the macrocycle accompanying distortion from planarity, (2) significant changes in the propane-1,3-diiminato chelate ring bonding patterns resulting from dihedral twists about its C–N bonds (Figure 4), and (3) perhaps diminished conjugation between the benzenoid moieties and the propane-1,3-diiminato chelate rings. While the solid-state spectrum of Ni($C_{22}H_{22}N_4$) is similar to its solution spectrum, the solid-state spectrum of Ni($C_{18}H_{14}N_4$) varies noticeably from its solution mate. This is probably a consequence of the packing of the planar molecule in the lattice (vide infra).

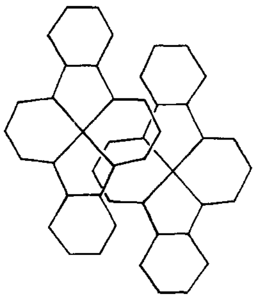

Figure 8. Projection in the molecular plane illustrating the overlap between adjacent molecules.

Packing of the Molecules

A stereodiagram of the contents of the unit cell is shown in Figure 6. In Figure 7 a stereodiagram containing several

Table V. Final Thermal Parameters for the Nonhydrogen Atoms in $Ni(C_{18}H_{14}N_4)^a$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A-Ni	0.001 55 (1)	0.018 03 (16)	0.002 55 (2)	0.000 59 (4)	0.000 84 (1)	0.000 23 (5)
A-N1	0.001 7 (1)	0.020 2 (7)	0.002 8 (1)	0.000 7 (2)	0.000 8 (1)	0.000 3 (2)
A-N2	0.001 7 (1)	0.020 6 (8)	0.002 8 (1)	0.000 4 (2)	0.001 0 (1)	0.000 0 (2)
A-C1	0.001 8 (1)	0.021 5 (8)	0.002 9 (1)	−0.000 4 (2)	0.001 1 (1)	0.000 3 (3)
A-C2	0.001 9 (1)	0.028 7 (10)	0.003 3 (1)	0.000 6 (2)	0.000 1 (1)	−0.000 3 (3)
A-C3	0.002 0 (1)	0.034 8 (12)	0.003 1 (1)	−0.000 1 (3)	0.000 6 (1)	−0.000 5 (3)
A-C4	0.002 5 (1)	0.029 2 (10)	0.003 3 (1)	−0.001 1 (3)	0.001 1 (1)	−0.002 3 (3)
A-C5	0.002 3 (1)	0.023 0 (9)	0.003 7 (1)	0.000 4 (2)	0.001 3 (1)	−0.001 2 (3)
A-C6	0.001 8 (1)	0.020 3 (9)	0.002 7 (1)	−0.000 2 (2)	0.001 0 (1)	0.000 6 (3)
A-C7	0.002 2 (1)	0.022 2 (9)	0.003 5 (1)	0.001 1 (2)	0.001 3 (1)	−0.000 4 (3)
A-C8	0.002 1 (1)	0.025 0 (9)	0.003 8 (1)	0.002 4 (2)	0.001 2 (1)	0.000 4 (3)
A-C9	0.001 8 (1)	0.025 5 (10)	0.003 3 (1)	0.001 3 (2)	0.000 8 (1)	0.001 4 (3)
B-Ni	0.001 60 (1)	0.021 48 (17)	0.002 61 (2)	−0.000 83 (4)	0.000 70 (1)	−0.000 07 (5)
B-N1	0.001 7 (1)	0.025 5 (8)	0.002 9 (1)	−0.000 9 (2)	0.000 9 (1)	0.000 1 (3)
B-N2	0.001 9 (1)	0.023 4 (8)	0.002 8 (1)	−0.000 8 (2)	0.000 7 (1)	−0.000 2 (2)
B-C1	0.002 0 (1)	0.024 6 (9)	0.002 8 (1)	0.000 3 (2)	0.000 8 (1)	0.001 8 (3)
B-C2	0.001 9 (1)	0.031 1 (11)	0.003 9 (1)	0.000 0 (2)	0.001 1 (1)	0.002 0 (3)
B-C3	0.002 4 (1)	0.038 4 (13)	0.004 4 (1)	0.002 6 (3)	0.001 8 (1)	0.003 7 (3)
B-C4	0.003 2 (1)	0.034 1 (11)	0.004 1 (1)	0.002 5 (3)	0.001 9 (1)	0.000 9 (3)
B-C5	0.002 8 (1)	0.026 6 (10)	0.003 7 (1)	0.000 2 (3)	0.001 3 (1)	−0.000 4 (3)
B-C6	0.002 0 (1)	0.023 9 (10)	0.002 8 (1)	0.000 4 (2)	0.000 9 (1)	0.001 2 (3)
B-C7	0.002 3 (1)	0.025 1 (10)	0.003 2 (1)	−0.001 1 (2)	0.000 7 (1)	−0.001 5 (3)
B-C8	0.002 2 (1)	0.028 6 (10)	0.003 7 (1)	−0.002 3 (2)	0.000 6 (1)	0.000 5 (3)
B-C9	0.001 8 (1)	0.031 3 (11)	0.003 8 (1)	−0.001 8 (2)	0.001 0 (1)	−0.000 0 (3)

[a] The form of the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; the number in parentheses following each datum is the estimated standard deviation in the last significant figure.

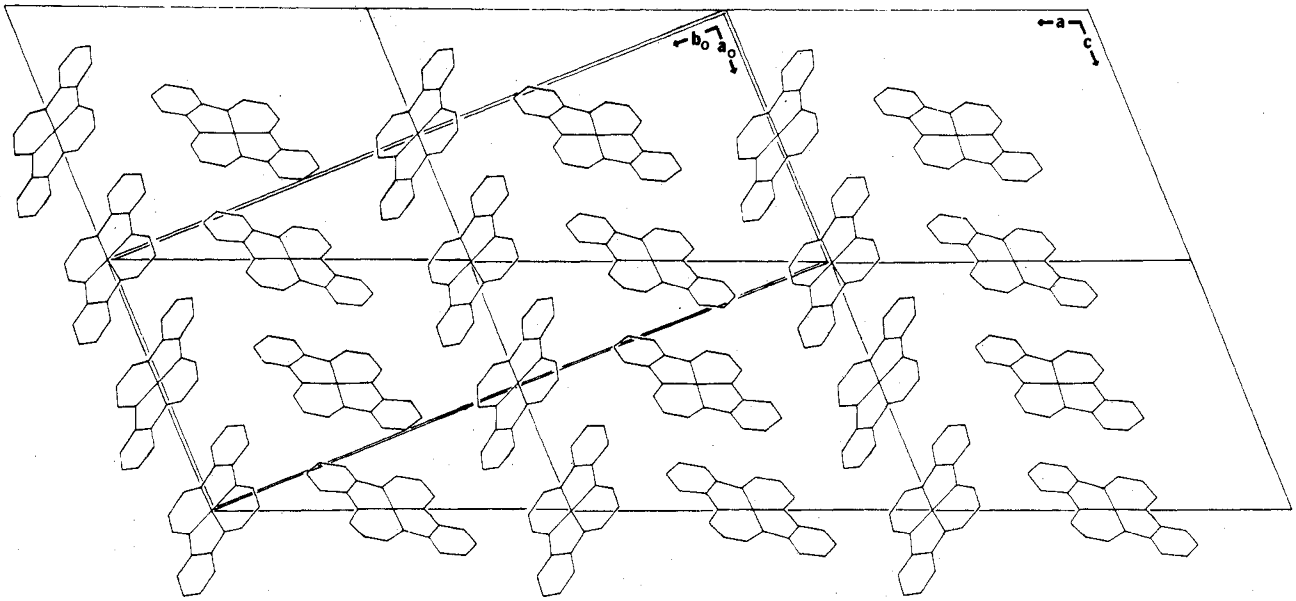

Figure 9. Projection down the *b* axis illustration the contents of several unit cells of $Ni(C_{18}H_{14}N_4)$ with the orthorhombic pseudostructure outlined.

unit cells is shown to display the molecular stacking. The individual molecules are stacked along the *b* axis resulting in a Ni–Ni separation of 5.228 Å, thus precluding any Ni–Ni interaction. However, the interplanar separations for molecules A and B of 3.235 and 3.295 Å, respectively, comparable to the interplanar separations in $Ni(dmg)_2$ (3.25 Å)[14] and graphite (3.35 Å),[16] are sufficiently close to account for the observed differences in the solution and solid-state spectra. These differences arise because of π–π and Ni–π interactions of adjacent stacked molecules. As can be seen in Figures 7 and 8, the significant overlap occurs between the six-membered propane-1,3-diiminato chelate rings on adjacent molecules with the nickel heteroatom approaching closest to C7 or C9. It is not obvious why the molecules do not stack along an axis perpendicular to the molecular plane as in $Ni(dmg)_2$.

The appearance of a pronounced pseudoorthorhombic pattern exhibited by the zero-level Weissenberg and precession photographs can be explained by examination of Figure 9. Outlined in the projection of the *ac* face of the $P2_1/c$ cell is the pseudoorthorhombic superstructure which zero-level photographs indicated as *Fddd* or *Fdd2* with $Z = 8$. The term "pseudo" is applied because γ_0 is 89.90° and the assignment of the orthorhombic space group is invalid because some atomic positions along the short axis $b = c_0 = 5.228$ Å are shifted relative to the positions required by *Fddd* or *Fdd2*. The original report of the synthesis and characterization of the metal complexes of the dibenzotetraaza[14]annulene contained an electron density map of $Ni(C_{18}N_{14}N_4)$, apparently obtained from a projection solution utilizing the orthorhombic cell.[5a]

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Registry No. Ni($C_{18}H_{14}N_4$), 22462-42-6; Co($C_{18}H_{14}N_4$), 22462-43-7; Ni($C_{22}H_{22}N_4$), 51223-51-9.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Bis(2-pyridine sulfinato)copper(II)

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The crystal and molecular structure of bis(2-pyridine sulfinato)copper(II), $CuC_{10}H_8N_2S_2O_4$, 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 0.028. The green monoclinic crystals form in the space group $P2_1/c$ with $a = 7.587$ (2) Å, $b = 10.106$ (3) Å, $c = 8.373$ (2) Å, $\beta = 114.08$ (2)°, and two molecules per unit cell. The tetragonally distorted octahedral Cu(II) ion lies at an inversion center where it is equatorially coordinated by two chelating 2-pyridine sulfinato ligands with Cu–N = 1.972 (2) Å and Cu–O = 1.957 (1) Å. The five-membered $\overline{\mathrm{CNCuOS}}$ chelate rings which form are nearly coplanar, with N–Cu–O = 85.20 (6)°. The remaining oxygen atoms of the ligands participate in axial approaches of 2.580 (2) Å to other Cu(II) ions; sulfinato is a bridging ligand. This compound is another product of the reaction of Cu(II) with organic disulfides to give copper(I) disulfide complexes and indicates that disulfides can be oxidized by Cu(II) in the presence of water, independent of the presence of O_2.

Introduction

Several copper(I) complexes of organic disulfides have been prepared and studied spectroscopically and crystallographically.[1-3] The reaction of bis(2-pyridyl) disulfide with $Cu(ClO_4)_2$ yielded a yellow precipitate (whose structure was subsequently determined by x-ray diffraction techniques to be a copper(I)–disulfide complex[3]) and a green product whose chemical analysis indicated that it could be a copper(II)–disulfide complex. This work was undertaken to learn its structure, to better understand the reaction of Cu(II) with organic disulfides.

Preparation Section

Cupric perchlorate hexahydrate, 99.9%, was obtained from Gallard-Schlessinger Chemical Manufacturing Corp. Bis(2-pyridyl) disulfide, trade name Aldrithiol-2, 98%, was obtained from Aldrich Chemical Co. and was recrystallized from ethanol–water as yellow needles (mp 57–58 °C). All other chemicals were of reagent grade quality. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared spectra were obtained using a Beckman IR-10 spectrometer.

Crystals were isolated by slow evaporation of a mixture of methanol solutions of cupric perchlorate hexahydrate and bis(2-pyridyl) disulfide in 1:1 and 1:2 ratios of the metal to the ligand. In the second preparation, the pH of the solution was checked periodically. Yellow and green crystals formed over a period of 2 weeks. The preparation was repeated successfully in a nitrogen atmosphere.

Anal. Calcd for the green product, $C_{10}H_8CuN_2O_4S_2$: C, 34.53; H, 2.32; Cu, 18.27; N, 8.05; O, 18.40; S, 18.43. Found: C, 34.60; H, 2.58; Cu, 17.77; N, 8.08; O (by difference), 18.30; S, 18.68.

Infrared Spectra

Infrared spectra of complexes containing the 2-pyridyl group have been studied.[4,5] The infrared spectrum of bis(2-pyridine sulfinato)copper(II), taken as a Nujol mull, has four ν(C=N), ν(C=C) bands at 1590, 1550, 1440, and 1418 cm^{-1}. The presence of only four bands indicates the approximate equivalence of the two pyridine rings.[5] The corresponding bands of bis(2-pyridyl) disulfide occur at 1568, 1552, 1440, and 1407 cm^{-1}, respectively. The shift of the 1568-cm^{-1} band to higher energy indicates coordination to the metal atom through the pyridine nitrogen. The ring-breathing mode, which appears in the disulfide at 980 cm^{-1}, is shifted to 1000 cm^{-1} in the complex and also indicates pyridine coordination.

The strong bands at 748 and 710 cm^{-1} in the disulfide are assigned to γ(C–H) and ϕ(C–C), respectively.[5] The γ(C–H) band occurs at 765 cm^{-1} in the complex, while the ϕ(C–C) band is split into two components at 712 and 700 cm^{-1}. A similar splitting has been observed in 2,2′-azopyridine complexes.[5]

The C–C out-of-plane deformation occurs at 460 cm^{-1} in the disulfide and is increased in frequency to 480 cm^{-1} in the complex, again indicating pyridine coordination. The presence of one band is indicative of a trans configuration of the pyridine rings.[5]

Sulfur–oxygen stretching vibrations have been studied.[6] Free gaseous sulfur dioxide has an antisymmetric stretch at 1362 cm^{-1} and a symmetric stretch at 1151 cm^{-1}.[7] These frequencies are shifted