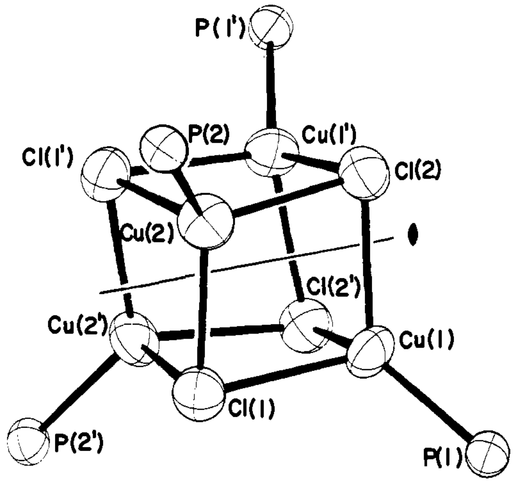

Figure 1. The "cubane" configuration of the Cu_4Cl_4 core of the $(PPh_3CuCl)_4$ molecule. The crystallographic C_2 axis is shown.

Å. Individual values (in Å) are Cu(1)···Cu(1') = 3.430 (2), Cu(2)···Cu(2') = 3.337 (2), Cu(1)···Cu(2) = Cu(1')···Cu(2') = 3.118 (1), and Cu(1)···Cu(2') = Cu(1')···Cu(2) = 3.417 (1). The Cl–Cu–Cl angles range from 88.94 (6) to 101.11 (7)°, while Cu–Cl–Cu angles range from 79.71 (6) to 90.19 (6)°. Each of the copper(I) atoms is in a distorted tetrahedral coordination environment; three linkages are to bridging chlorine atoms, the fourth being to a triphenylphosphine ligand. Individual copper–phosphorus bond distances are Cu(1)–P(1) = Cu(1')–P(1') = 2.193 (2) and Cu(2)–P(2) = Cu(2')–P(2') = 2.192 (3) Å.

$(PPh_3CuBr)_4$ was prepared following the procedure of Jardine, *et al.*;[10] it was recrystallized from chloroform, and was isolated as the solvated species $(PPh_3CuBr)_4 \cdot 2CHCl_3$.[11] Crystals belong to the centrosymmetric monoclinic space group $C2/c$ (No. 15; C_{2h}^6), unit cell parameters being a = 28.461 (9), b = 15.983 (4), c = 18.044 (5) Å, β = 112.59 (2)°, and Z = 4. Data collection and structure solution were as for the chloro derivative (*vide supra*). All nonhydrogen atoms have been accurately located, the present discrepancy indices being $R_F = 7.7\%$ and $R_{wF} = 8.5\%$ for the 2412 independent refections representing data complete to $2\theta = 35°$ (Mo Kα radiation). The $(PPh_3CuBr)_4$ molecule has precise (*i.e.*, crystallographically dictated) C_i ($\bar{1}$) symmetry, with the Cu_4Br_4 core having a "step" configuration (see Figure 2).

It should be emphasized that this molecule contains copper(I) atoms in both tetrahedral (Cu(1) and Cu(1')) and trigonal planar ((Cu(2) and Cu(2')) coordination environments.

The ten edges of the Cu_4Br_4 "step" are each defined by a Cu–Br bond. While these bond lengths show considerable variation, a systematic pattern can be ascertained, *i.e.*, the higher the coordination numbers (CN's) of the atoms involved in the Cu–Br bond, the longer the bond will be. Thus, in order of increasing bond distance, Cu(2)–Br(1') = Cu(2')–Br(1) = 2.374 (3) Å (CN's 3 and 2); Cu(2)–Br(2) = Cu(2')–Br(2') = 2.429 (3) Å (CN's 3 and 3); Cu(1)–Br(1) = Cu(1')–Br(1') = 2.477 (3) Å (CN's 4 and 2); Cu(1)–Br(2) = Cu(1')–Br(2') = 2.527 (2) Å (CN's 4 and 3); and Cu(1)–Br(2') = Cu(1')–Br(2) = 2.662 (2) Å (CN's 4 and 3). Copper–copper distances are Cu(1)···Cu(1') = 3.449 (2) Å and Cu(1)···Cu(2') = Cu(1')···Cu(2) = 2.989 (3) Å. Lastly we may note that the Cu(tetrahedral)–P distances, Cu(1)–P(1) = Cu(1')–P(1') = 2.207 (4) Å, are slightly longer than the Cu(trigonal)–P distances, Cu(2)–P(2) = Cu(2')–P(2') = 2.200 (5) Å.

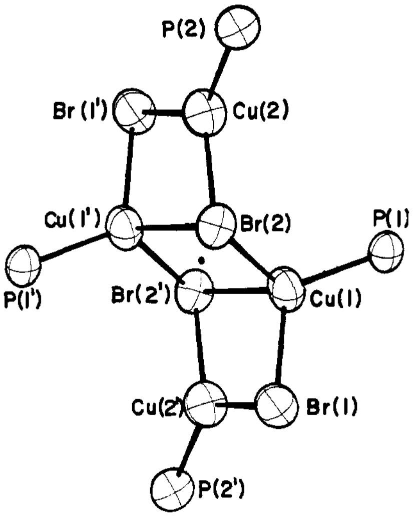

Figure 2. The "step" configuration of the Cu_4Br_4 core in crystalline $(PPh_3CuBr)_4 \cdot 2CHCl_3$. The center of symmetry is indicated by a solid circle.

The gross geometry of the Cu_4Br_4 core may be described in terms of the dihedral angle of 107.70° between the strictly planar system Br(2)–Cu(1)–Br(2')–Cu(1') and the approximately planar (rms deviation 0.07 Å) system Br(2)–Cu(2)–Br(1')–Cu(1').

The relationship between the "cubane" and "step" structures is self-evident (*cf.* Figures 1 and 2). Spectroscopic and diffraction studies presently in progress should lead to our determining the gross geometry of the Cu_4X_4 (X = halogen or other monodentate ligand of unit negative charge) cores of related phosphine and arsine complexes of copper(I) and to our elucidating the conditions under which the "cubane" and "step" structures will interconvert.

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Crystal and Molecular Structure of an Octaaza[14]annulene Complex of Nickel(II)

Sir:

The concept of aromaticity and its congeners denoted by prefixes such as anti, quasi, and pseudo continues

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(10) F. H. Jardine, L. Rule, and A. G. Vohra, *J. Chem. Soc. A*, 238 (1970).

(11) This formulation assumes 100% occupancy of the eightfold (general) chloroform sites. In fact, both refinement of occupancy factors and accurate density measurements suggest that the true stoichiometry *of our particular sample* is close to $(PPh_3CuBr)_4 \cdot 1.5CHCl_3$.

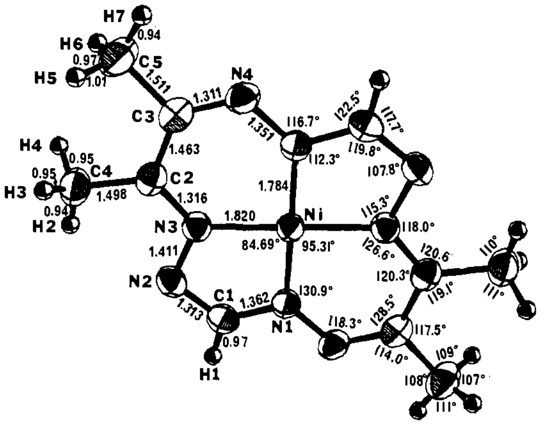
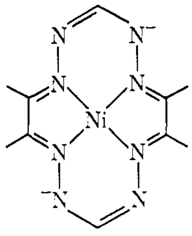


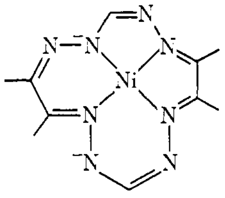
Figure 1. Molecular structure and labeling scheme of the dihydrooctaaza[14]annulene nickel(II) complex. The left side of the drawing shows the bond lengths and the right side illustrates selected bond angles. The estimated standard deviations are as follows: Ni-N distances, 0.001 Å; C-C and C-N distances, 0.002-0.003 Å; C-H distances, 0.02 Å; angles involving Ni, 0.06°; angles involving nonhydrogen light atoms, 0.1°.

to fascinate many chemists.[1] Similarly, the influence of metal atoms on the degree of double bond fixation and reactivity of unsaturated ligands has been a frequent subject of investigation. In recent years, a number of transition metal complexes of macrocyclic ligands containing completely conjugated π-electron systems have been isolated. We have isolated a number of complexes of aza analogs of [14]annulene transition metal complexes and wish to report our results on the three-dimensional crystal structure of a 16π-electron system, an octaaza[14]annulene nickel(II) complex.

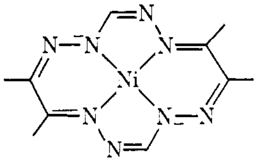
The condensation of 2,3-butanedione, hydrazine, and formaldehyde with nickel(II) perchlorate under the appropriate conditions yields three geometrical isomers of a molecular nickel(II) complex of 3,4,10,11-tetramethyl-1,2,5,6,8,9,12,13-octaaza[14]annulene, I, II, and III.[2,3] Isomer III is the most stable; both I and II are irreversibly converted to III by heating.[4]



I

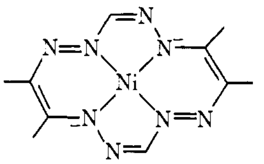


II

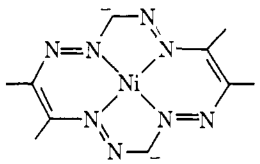


III

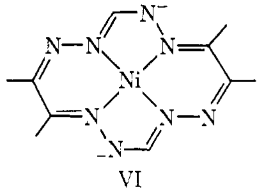
The macrocyclic ligand of each isomer is a dianionic ligand containing a 16π-electron system and each can be represented by a number of valence isomers. For example, IV, V, and VI are valence isomers of III.



IV



V



VI

The three-dimensional crystal structure of the complex of C_{2h} symmetry was undertaken to provide answers to the following questions. What is the extent of delocalization in this completely conjugated macrocyclic ligand complex? What is the arrangement of double bonds and negative charges if a localized bond structure is found? Is the macrocyclic ligand exerting a constricting effect on the metal ion? Why is the C_{2h} structure preferred over the more symmetrical D_{2h} structure?

Recrystallization of III from boiling nitroethane yields a mixture of crystals belonging to the orthorhombic and triclinic systems. The crystals with the triclinic space group were most suitable for data collection: $a = 8.433$ (1), $b = 8.408$ (2), $c = 4.8600$ (8) Å; $\alpha = 75.94$ (1), $\beta = 68.25$ (1), $\gamma = 81.73$ (1)°; $\rho_{\text{calcd}} = 1.632$ g/cm^3, $\rho_{\text{exptl}} = 1.628$; $Z = 1$. A total of 1135 independent reflections were measured on a Picker-FACS-1 diffractometer and 961 unique reflections with $F > 2\sigma$ were used in the structural refinement. The nickel(II) atom was placed at the origin of the unit cell with the assumption that the space group was $P\bar{1}$. All the remaining atoms were located by successive least squares and difference Fourier techniques. Refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms and with isotropic thermal parameters for the hydrogen atoms converged to a final $R = 2.21$ ($R_w = 2.73$). See paragraph at end of paper regarding supplementary material.

The molecular structure and labeling scheme of $NiC_{10}H_{11}N_8$ together with the distances and angles are presented in Figure 1. The ligand is essentially planar; the largest displacements from the least squares of the ring are only 0.01 Å. The carbon atoms C(4) and C(5) of the methyl groups are slightly out of the plane, -0.04 and 0.05 Å, respectively, because of the nonbonding H-H interactions of the $-CH_3$ groups. Thus, the molecule has only rigorous C_i symmetry in this crystal structure.

The C-C and N-N distances (Figure 1) clearly indicate that the ligand has an alternating double bond structure which is best described by the tautomeric form III. The structure has distances which are consistent with a conjugated system containing some double

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(1) Ernst D. Bergmann and Bernard Pullman, Ed., "Aromaticity, Pseudo-aromaticity and Anti-aromaticity," Academic Press, New York, N. Y., 1971.

(2) V. L. Goedken and S.-M. Peng, *J. Chem. Soc., Chem. Commun.*, 62 (1973).

(3) Similar complexes of C_{2h} symmetry have been prepared by the insertion of divalent transition metal ions into macrocyclic ligands formed by the condensation of bishydrazones with ortho esters: J. E. Baldwin, R. H. Holm, R. W. Harper, J. Huff, S. Koch, and T. J. Truex, *Inorg. Nucl. Chem. Lett.*, **8**, 393 (1972).

(4) The structures of I and II are drawn to indicate the degree of unsaturation present. Each isomer may have a double bond arrangement which differs from that of the valence tautomers shown.

bond delocalization, about 20%, but militate against describing the structure as aromatic. These distances may be compared with those of [14]annulene and [16]-annulene originally prepared by Sondheimer[5,6] and structurally elucidated by Paul.[7,8] The alternation of bond lengths observed in the 16π-electron system of our dihydrooctaaza[14]annulene complex are very similar to those observed in [16]annulene, which, however, is markedly nonplanar.[8] The bond lengths found in the structure of [14]annulene are essentially equivalent and consistent with aromatic character.

The double bonds, C(1)–N(2), N(3)–C(2), and C(3)–N(4), have distances of 1.313 (2), 1.316 (2), and 1.311 (2) Å, respectively, which are only slightly longer than those found in complexes having isolated imine linkages.[9] Supporting this alternating double bond arrangement is the C(2)–C(3) distance of 1.463 (2) Å which is slightly greater than the 1.435 (7) Å found in the bisglyoximato nickel(II) complex.[10] With this disposition of double bonds, the negative charges of the ligand formally reside on N(1) and N(1)′, a location which most effectively neutralizes the positive charge on nickel(II). This charge localization is probably responsible for the Ni–N(1) distance, 1.784 (1) Å being significantly shorter than normal for low-spin Ni(II)–N distances and even shorter than those found in the 13-membered ring macrocyclic nickel(II) complex, 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,12-dienatonickel(II) perchlorate.[11] Similarly the "bites" of the five- and six-membered chelate rings N(1)–N(3) = 2.428 Å and N(3)–N(1)′ = 2.664 Å are shorter than normal and indicate some degree of constriction of the nickel(II) by the highly conjugated ligand.

The greater stability of the C_{2h} structure, III, over the more symmetrical D_{2h} structure can be rationalized on the basis of the arguments given by Nyholm and Gillespie[12] and from the fact that the interior angles of five-membered chelate rings are smaller than those of six-membered chelate rings. The angles defined by C(1)=N(2)—N(4) and C(3)=N(4)—N(1)′, where N(2) and N(4) each contain a lone pair of electrons, are predicted to be less than 120°. In the five-membered rings, a comparatively small angle of 107.8° is observed for the atoms C(1)=N(2)—N(3) whereas a much larger angle of 118.3° is observed for the atoms C(3)=N(4)—N(1) in the six-membered rings. The angular strain of the D_{2h} structure which contains four C–N–N angles close to 120° can be relieved by the observed isomerization to the C_{2h} structure thereby incorporating two of the C–N–N angles into the five-membered chelate rings. It should be noted that a sharp angle, 111°, has also been recently observed for the N–N–C angle of a similar five-membered chelate ring formed by the addition of hydrazine to platinum(II) nitriles followed by air oxidation.[13]

Acknowledgment. We thank Dr. Joseph Pluth for his assistance with the data reduction. This research was partially supported by a grant from the National Institutes of Health, No. NL-4827.

Supplementary Material Available. A listing of atomic coordinates and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-5773.

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(5) F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **82**, 5765 (1960).

(6) F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, **83**, 4863 (1961); I. C. Calder, Y. Gaoni, and F. Sondheimer, *ibid.*, **90**, 4946 (1968).

(7) C. C. Chiang and I. C. Paul, *J. Amer. Chem. Soc.*, **94**, 4741 (1972).

(8) S. M. Johnson, I. C. Paul, and G. S. D. King, *J. Chem. Soc. B*, 643 (1970).

(9) R. W. G. Wyckoff, "Crystal Structures," Vol. VI, Wiley, New York, N. Y., 1969, p 243; B. T. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc.*, 2407 (1969).

(10) M. Calleri, G. Ferrario, and D. Viterbo, *Acta Crystallogr.*, **22**, 468 (1967).

(11) M. F. Richardson and R. E. Sievers, *J. Amer. Chem. Soc.*, **94** 4134 (1972).

(12) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **11**, 339 (1957); R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963); R. J. Gillespie, *Angew. Chem.*, **6**, 819 (1967).

(13) R. Mason, K. M. Thomas, A. R. Galbraith, and B. Shaw, *J. Chem. Soc., Chem. Commun.*, 297 (1973).

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Structure of a Transition Metal Dicyanovinylidene Complex, $(C_5H_5)Mo[C{=}C(CN)_2][P(OCH_3)_3]_2Cl$

Sir:

Recently the reactions between the 1-chloro-2,2-dicyanovinylidenemolybdenum and -tungsten derivatives $[(NC)_2C{=}C(Cl)]M(CO)_3(C_5H_5)$ (where M = Mo and W) and trivalent phosphorus ligands were reported[1,2] to give complexes of the type $(C_5H_5)M[C{=}C(CN)_2](PR_3)_2Cl$ in which a novel terminal dicyanovinylidene (or dicyanomethylene carbene) ligand is formed by an unusual chloride migration from carbon to molybdenum. The dicyanovinylidene ligand is of particular interest because of its relationship to the carbonyl ligand by substitution of an oxygen atom with an isoelectronic dicyanomethylene group.[1-5] This communication reports the first structural details on such a transition metal dicyanovinylidene complex.

The compound $(C_5H_5)Mo[C{=}C(CN)_2][P(OCH_3)_3]_2Cl$ was recrystalized from a mixture of dichloromethane and hexane to give clear orange, square rods in the monoclinic space group C_{2h}^5-$P2_1/n$. The unit cell contains four molecules and has dimensions $a = 9.127$ (2) Å, $b = 18.515$ (2) Å, $c = 12.923$ (2) Å, and $\beta = 91.56$ (1)°. A total of 3037 absorption-corrected structure amplitudes with $F_o^2 > 3\sigma(F_o^2)$ were used in the solution and refinement of the structure. Hydrogen atoms were located on a difference Fourier synthesis and were included in the refinement as a fixed-atom structure factor contribution. The final cycle of anisotropic full-matrix least-squares refinement led

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(1) R. B. King and M. S. Saran, *J. Chem. Soc., Chem. Commun.*, 1053 (1972).

(2) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1817 (1973).

(3) R. B. King, *Inorg. Nucl. Chem. Lett.*, **9**, 457 (1973).

(4) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **94**, 1784 (1972).

(5) R. B. King and M. S. Saran, *J. Amer. Chem. Soc.*, **95**, 1811 (1973).