temperatures and resonance separations at low temperature in ^{13}C and ^{1}H spectra, respectively, are 15 ± 1 kcal/mol in aqueous solution and 13 ± 1 kcal/mol in DMSO–CD_2Cl_2 solution.

cyclo(L-Pro-Gly)$_2$ is likely to adopt the cis–trans–cis–trans peptide bond backbone (with two cis Gly-Pro bonds),[2–13] which has been consistently found by Dale and Titlestad in sarcosine-containing cyclic tetrapeptides.[21–23] ^{13}C spectra have shown in several instances that the Pro C_γ resonance is the most sensitive and reliable indicator of a change in the conformational state of the X-Pro peptide bond,[10,16–19] but in *cyclo*(L-Pro-Gly)$_2$ spectra (Figure 1), Pro C_γ remains at the position attributed to cis peptide bonds (*ca.* 171 ppm). Furthermore, in contrast to the $\Delta F^{\ddagger}$ values calculated above, typical values for cis–trans isomerism of unhindered amides are in the range of 20 ± 1 kcal/mol.[24] Models indicate that interconversion between the cis′ and trans′ forms of the Pro-Gly units may be sterically difficult (due to transannular contacts) and might be expected to be "slow" on the nmr time scale. The foregoing data lead to the suggestion that the two Pro-Gly units differ by the orientation of the amide linkage joining the Pro and Gly residues (*i.e.*, by rotations about the Pro ψ and succeeding Gly ϕ angles). The nmr data are in accord with such an asymmetric conformation of *cyclo*(L-Pro-Gly)$_2$, containing the cis–trans–cis–trans peptide bond backbone,[21–23,25] but having one cis′ and one trans′ Pro C_α–C=O bond[26] (as shown schematically in Figure 3).

Preliminary nmr studies on two other cyclic tetrapeptides synthesized in this laboratory—*cyclo*(D-Pro-Gly-L-Pro-Gly) (see ref 1) and *cyclo*(L-Pro-Sar)$_2$—indicate no coalescence behavior in nmr spectra obtained under solvent and temperature conditions similar to those used for *cyclo*(L-Pro-Gly)$_2$. The ^{13}C chemical shift of the Pro C_γ resonance of each of the two latter peptides is in the region ascribed to cis X-Pro peptide bonds, providing evidence that the cis–trans–cis–trans peptide backbone again prevails in these molecules.

The results obtained herein for *cyclo*(L-Pro-Gly)$_2$ suggest that, in cases where comparable steric hindrance is absent (*e.g.*, in larger cyclic peptides and in linear peptides), cis′–trans′ interconversion is likely to be considerably faster.

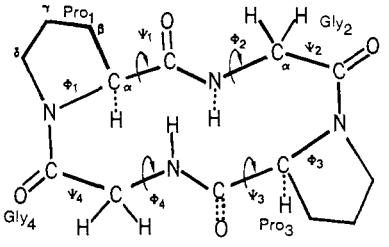

Figure 3. A diagrammatic representation of the asymmetric conformation proposed for *cyclo*(L-Pro-Gly)$_2$ in solution. The dotted bonds extend below the plane of the paper. Gly$_4$-Pro$_1$ and Gly$_2$-Pro$_3$ peptide bonds are cis; Pro$_1$-Gly$_2$ and Pro$_3$-Gly$_4$ peptide bonds are trans. The Pro$_1$ ψ_1 angle is trans′, and the Pro$_3$ ψ_3 angle is cis′. Interconversion with the identical conformer but with ψ_1 cis′ and ψ_3 trans′ occurs by rotation of the amide unit joining Pro$_1$ and Gly$_2$ (about the bonds denoted by arrows), with the N–H proton passing through the interior of the cyclic peptide ring and a similar rotation of the Pro$_3$—Gly$_4$ amide unit.

(21) J. Dale and K. Titlestad, *Chem. Commun.*, 656 (1969).
(22) J. Dale and K. Titlestad, *Chem. Commun.*, 1403 (1970).
(23) J. Dale and K. Titlestad, *J. Chem. Soc., Chem. Commun.*, 255 (1972).
(24) W. E. Stewart and T. H. Siddall, III, *Chem. Rev.*, 70, 517 (1970).
(25) J. Konnert and I. L. Karle, *J. Amer. Chem. Soc.*, 91, 4888 (1969).
(26) One cannot exclude an alternative interpretation of the data reported here, namely, that the observed asymmetric conformation of *cyclo*(L-Pro-Gly)$_2$ has a cis–trans–trans–trans peptide backbone with one cis and one trans Gly-Pro peptide bond. (Pro ψ angles could then not be specified from the nmr data.) Models indicate that such a structure would have one highly nonplanar Gly-Pro peptide bond, distorted *ca.* 40° from planarity. The higher ground state energy expected for such a conformer would account for the observed low interconversion barrier. While the cis–trans–cis–trans conformer proposed in the text is calculated to be the lower energy structure by 2–3 kcal/mol, the predictive power of the calculation is not sufficient to exclude the higher energy cis–trans–trans–trans conformer. (V. Madison, this laboratory, personal communication.)

Acknowledgments. This work has been supported, in part, by U.S. Public Health Service Grants AM07300 and AM10794. We thank the National Science Foundation (under Grant GB-41535) for providing major support for a ^{13}C spectrometer, the Muscular Dystrophy Association of America for a fellowship (to E. T. F.), and the Department of Chemistry for the use of the Varian XL-100-15 nmr instrument (provided by the National Science Foundation under Grant GP-32317). We are grateful to Dr. Vincent Madison for several stimulating discussions.

Charles M. Deber, Eric T. Fossel, Elkan R. Blout*
Department of Biological Chemistry, Harvard Medical School
Boston, Massachusetts 02115
Received February 25, 1974

Synthesis, Structure, and Bonding of a Cubane-Like Cobalt–Nitrosyl Complex, $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$. Stereochemical Nonconformity of the Metal Cluster Geometry to That Predicted by a First-Order Jahn–Teller Effect

Sir:

A concentrated synthetic and stereochemical investigation of cubane-like metal clusters for the purpose of correlating the detailed changes in geometry with different MO-electronic configurations[1] has resulted in the preparation and characterization of $Co_4(NO)_4(\mu_3\text{-}NR)_4$ (where R = $C(CH_3)_3$). This metal nitrosyl tetramer is of prime interest not only in being the first characterized cubane-like molecule in which the metal atoms are each coordinated to a nitrosyl group as a single terminal ligand but also in representing the first such case for a metal cluster system in which its presumed idealized geometry does not conform to that expected from considerations of the first-order Jahn–Teller effect.

The successful synthesis of a metal cluster $M_4(NO)_4(\mu_3\text{-}X)_4$ system was accomplished by the reaction of $Co(NO)(CO)_2P(C_6H_5)_3$ with excess $\{(CH_3)_3CN\}_2S$ in refluxing toluene which produced a very soluble brown crystalline complex isolated in small yields (5–10%) from other products. Elemental analysis together with a parent ion peak at *m/e* 640 in its mass spectrum provided the initial evidence for the tetrameric nature of $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$. A solid-state infrared spectrum (KBr pellet) exhibits a single strong nitrosyl band at 1722 cm^{-1} in accord with one terminal nitrosyl

(1) (a) G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, **95**, 2164 (1973), and references cited therein; (b) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 3389 (1972); (c) B. K. Teo and L. F. Dahl, to be submitted for publication.

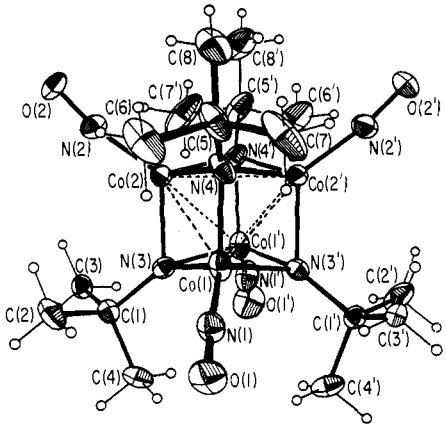

Figure 1. The cubane-like $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$ molecule with crystallographic site symmetry C_2-2 is drawn with 15% probability thermal ellipsoids for the nonhydrogen atoms.

ligand per cobalt atom. The diamagnetism of this air-stable complex was established from the observation of a sharp proton singlet in CCl_4 solution at τ 8.83 (*vs.* internal TMS).

Our particular interest in obtaining either this complex or the (as yet) unknown electronically equivalent $Co_4(NO)_4(\mu_3\text{-}S)_4$ one for an examination by X-ray diffraction stemmed from the fact that simple electron bookkeeping indicates the likelihood of a cubane-like architecture with a MO-electronic configuration different from any of the previously characterized cubane-like metal complexes; *i.e.*, in order for each cobalt atom to achieve a so-called closed-shell configuration, four electron-pair bonding and two nonbonding metal–metal interactions are predicted (from a localized valence-bond viewpoint).

A resulting structural determination[2,3] showed that the $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$ molecule (Figure 1) indeed possesses a cubane-like framework with the triply bridging NR ligands situated above the four triangular faces of the cobalt tetrahedron such that the cobalt and nitrogen atoms occupy alternate corners of a distorted cube. The salient structural feature is that the entire molecule, which conforms exactly to C_2-2 site symmetry, experimentally possesses an orthorhombic D_2-222 geometry. The six Co–Co distances divide under D_2 symmetry into three distinct pairs with one pair of identical length 2.460 (2) Å, a second pair of identical length 2.544 (2) Å, and a third pair of lengths 2.701 (3) and 2.717 (2) Å. This observed distortion of the Co_4N_4 core from a cubic T_d geometry toward an orthorhombic D_2 one is also evidenced by: (1) the four independent N···N distances of the nonbonding tetrahedron of nitrogen atoms being 2.83 (1), 2.89 (1), 2.67 (1), and 2.68 (1) Å, of which the last two are chemically equivalent; (2) the 12 Co–N–Co bond angles (of which six are crystallographically independent) separating into three distinct chemically equivalent pairs of 80.2 (3) and 81.3 (3)°, of 83.9 (3) and 84.1 (3)°, and of 89.5 (3) and 89.6 (3)°; and (3) the six crystallographically independent N–Co–N bond angles likewise breaking down into three chemically equivalent pairs of 88.2 (3) and 88.3 (3)°, of 95.6 (2) and 96.3 (3)°, and of 98.6 (3) and 99.6 (4)°. The 12 Co–N bond lengths (of which six are independent) of range 1.87 (1)–1.94 (1) Å do not reflect this orthorhombic distortion in their breakdown under assumed D_2 symmetry into three sets with mean values 1.88, 1.92, and 1.92 Å. The two crystallographically independent (but chemically equivalent) nitrosyl ligands give rise to Co–NO lengths of 1.645 (9) and 1.662 (10) Å, to N–O lengths of 1.16 (1) and 1.15 (1) Å, and to Co–N–O bond angles of 174 (1) and 168 (1)°.

On the basis that the two longer Co–Co distances represent nonbonding metal–metal interactions, each of the four shorter Co–Co distances is then presumed under the utilized metal cluster model to reflect (in a localized sense) an electron-pair bond (of bond order 1.0) thereby resulting in a total limiting Co–Co valence bond order of 4.0 (*i.e.*, corresponding to 12 bonding and four antibonding electrons directly involved in the tetracobalt interactions). This description is in harmony with each cobalt atom achieving a noble-gas magic number. However, the highly delocalized nature of the tetrametal cluster orbitals in a cubane-like $M_4L_4(\mu_3\text{-}X)_4$ system does not make it necessary from the application of a qualitative MO metal cluster model to gauge from the determined differences in Co–Co distances the extent of localization of these antibonding electrons between the pairs of metal atoms. That the two longer Co–Co distances of 2.709 Å (av) are too short to be considered unambiguously as nonbonding is taken as an indication that the metal cluster orbitals housing the four antibonding electrons are not purely antibonding between only two pairs of cobalt atoms.

In order to rationalize the observed orthorhombic D_2 distortion in the geometry of the Co_4N_4 core from an idealized cubic T_d geometry, a simple qualitative MO metal cluster model is invoked. Due primarily to the ability of NO to function as a π-acidic ligand, the overall MO scheme for $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$ is similar to that previously utilized[1c] for the cubane-like organometallic molecules (*e.g.*, $M_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}X)_4$ where M = Fe, X = S,[4a,b] M = Co, X = S,[1a] and M = Co, X = P[4c]). Of the available 64 valence electrons, 32 occupy the low-lying *bonding* σ-like metal–ligand levels and another 16 occupy the ($e + t_1 + t_2$) levels comprised largely of metal d orbitals which are essentially nonbonding with respect to direct Co–Co interactions but which are strongly stabilized by metal–nitrosyl back-bonding involving the π^*(NO) orbitals. Twelve of the remaining 16 electrons fill the six *bonding* tetracobalt ($a_1 + e + t_2$) levels, while the other four electrons would occupy (under assumed T_d geometry) the *antibonding* ($t_1 + t_2$) tetracobalt combinations. Such a sixteen-electron system is predicted[1c] to distort to a tetragonal D_{2d}-$\bar{4}2m$ geometry *via* a Jahn–Teller active vibration giving rise to a tetracobalt architecture

(2) $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$: tetragonal, $P4_12_12$; $a = b = 11.725$ (7), $c = 20.606$ (5) Å; $V = 2832.8$ Å^3; $\rho_{calcd} = 1.50$ g cm^{-3} for $Z = 4$. Anisotropic least-squares refinement including anomalous dispersion gave $R_1(F) = 4.2\%$ and $R_2(F) = 4.6\%$ for 861 independent diffractometry data ($I > 2\sigma(I)$). The origin was shifted down by $^1/_8$ in the z direction from that given for $P4_12_12$ in "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 182. The resulting general positions are: x, y, z; $-x, -y, {}^1/_2 + z$; ${}^1/_2 - y, {}^1/_2 + x, {}^1/_4 + z$; ${}^1/_2 + y, {}^1/_2 - x, {}^3/_4 + z$; $y, x, {}^3/_4 - z$; $-y, -x, {}^1/_4 - z$; ${}^1/_2 - x, {}^1/_2 + y, -z$; ${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 - z$.

(3) For computation of distances and bond angles, atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal.

(4) (a) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966); (b) C. H. Wei, R. G. Wilkes, P. M. Treichel, and L. F. Dahl, *ibid.*, **5**, 900 (1966); (c) G. L. Simon and L. F. Dahl, *J. Amer. Chem. Soc.*, **95**, 2175 (1973).

with four short equivalent Co–Co bonds and two longer equivalent Co–Co bonds. Hence, the nonconformity of the Co_4N_4 core to a tetragonal D_{2d} geometry with four equivalent short Co–Co distances is *not* consistent with the predicted first-order Jahn–Teller effect.[5]

The close resemblance of the structural parameters of $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$ to an orthorhombic D_2 geometry is indicative that effects more systematic than those of anisotropic crystal-packing forces or internal intramolecular steric pressures are operative in this case to produce the observed deviations from the predicted D_{2d} geometry.[6,7] The weak second-order Jahn–Teller effect[8] can produce perturbations on molecular geometry by vibronic coupling of the ground state and low-lying excited states of the same spin multiplicity. Both Pearson[9] and Mingos[10] have utilized the second-order Jahn–Teller effect to rationalize the structures of molecules. The vibrations which can produce such a second-order distortion must be contained in the direct product of the symmetry species of the ground and excited states. On the basis of the reasonable assumption that a first-order Jahn–Teller mechanism has provided a tetragonal D_{2d} geometry such that the HOMO containing the four antibonding metal clusters electrons is a doubly degenerate e orbital and with higher unoccupied b_2, e, and a_2 *antibonding* MO's, only the direct product e $\times$ e contains the B_1 mode which is the normal mode of vibration consistent with a deformation from D_{2d} to D_2 geometry.

The plausibility of these qualitative arguments is contingent upon a quantitative approach to the bonding in $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$.[11,12] Whether the D_2 geometry, instead of the D_{2d} one expected for a system of this particular MO-electronic configuration, is unique to this molecule or is also characteristic of other electronically equivalent cubane-like systems must await further structural studies. In this connection a vigorous effort is being made to prepare the unknown $Co_4(NO)_4(\mu_3\text{-}S)_4$ analog. The work presented here will be reported in full upon completion of closely related research which will include the characterization of the recently prepared monocation of $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$ as well as the preparation and structural analysis of the cubane-like $Co_4(NO)_4(\mu_3\text{-}NR)_3(\mu_3\text{-}SNR)$ molecule (where R = $C(CH_3)_3$), a unique complex involving the replacement of one NR ligand with a SNR ligand which is also electronically equivalent to a triply bridging disulfide ligand.

Acknowledgments. We are most grateful to the donors of the Petroleum Research Fund, administered by American Chemical Society, and to the National Science Foundation (No. GP-19175X) for their financial support including a postdoctoral research position for N. G. C. (Department of Inorganic Chemistry, University of Bristol). The use of the UNIVAC 1108 computer at the Academic Computing Center, University of Wisconsin (Madison), was made available through partial support of the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee. Special thanks are given to Dr. Boon Keng Teo at Bell Laboratories (Murray Hill) for helpful consultations.

Supplementary Material Available. A listing of atomic coordinates 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 $\times$ 148 mm, 24$\times$ 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-74-4017.

Robert S. Gall, Neil G. Connelly, Lawrence F. Dahl*
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706
Received February 14, 1974

(5) R. W. Jotham and S. F. A. Kettle, *Inorg. Chim. Acta*, **5**, 183 (1971). A distortion from a cubic T_d to a tetragonal D_{2d} geometry *via* an E mode vibration is possible as the E representation in T_d correlates with the totally symmetric A_1 representation under tetragonal D_{2d} symmetry. However, a distortion from a cubic T_d to an orthorhombic D_2 geometry is not allowed by the first-order Jahn–Teller effect, even though the E representation of T_d symmetry correlates with the (A + A) representation under D_2 symmetry, due to the tetragonal D_{2d} point group being an intermediate point group.

(6) Considerable variations of 0.1 Å in metal–metal distances have been observed in the solid state for cubane-like tetramers containing a nonbonding tetrahedron of metal atoms (*e.g.*, $Co_4(\eta\text{-}C_5H_5)_4(\mu_3\text{-}S)_4$,[1a] $Os_4(CO)_{12}(\mu_3\text{-}O)_4$,[7a] and $Re_4(CO)_{12}(\mu_3\text{-}SCH_3)_4$[7b]). Although the observed differences in the nonbonding metal–metal distances in each of these molecules are statistically significant, there is no *chemical* significance in the observed nonsystematic variations from an idealized cubic T_d geometry aside from the presumed anisotropic steric effects. It has been pointed out[1a] that maximum variations are expected and found for metal–metal distances for which the *net* metal–metal interactions are nonbonding. In the case of $Co_4(NO)_4(\mu_2\text{-}NC(CH_3)_3)_4$ it is presumed from potential energy considerations that the metal–metal bonding (manifested by the short Co–Co distances) would lead to a relatively rigid Co_4N_4 core for which it then is difficult to reconcile the observed D_2 deformation from a tetragonal D_{2d} geometry as arising from only interligand repulsions (with complete neglect of electronic effects).

(7) (a) D. Bright, *Chem. Commun.*, 1169 (1970); (b) E. W. Abel, W. Harrison, R. A. N. McLean, W. C. Marsh, and J. Trotter, *ibid.*, 1531 (1970); W. Harrison, W. C. Marsh, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1009 (1972).

(8) (a) U. Öpik and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **238**, 425 (1957); (b) R. F. W. Bader, *Can. J. Chem.*, 40, 1164 (1962).

(9) R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

(10) D. M. P. Mingos, *Nature (London), Phys. Sci.*, **229**, 193 (1971).

(11) Molecular orbital calculations of these metal cluster systems (including the terminal ligands) are being performed *via* the nonparameterized Fenske–Hall model[12] in order to determine the degree of validity of our currently utilized qualitative metal cluster model (which allows complete electron delocalization only among the metal atoms).

(12) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 768 (1972).

Preparation, Structure, and Bonding of Two Cubane-Like Iron–Nitrosyl Complexes, $Fe_4(NO)_4(\mu_3\text{-}S)_4$ and $Fe_4(NO)_4(\mu_3\text{-}S)_2(\mu_3\text{-}NC(CH_3)_3)_2$. Stereochemical Consequences of Bridging Ligand Substitution on a Completely Bonding Tetrametal Cluster Unit and of Different Terminal Ligands on the Cubane-Like Fe_4S_4 Core

Sir:

We wish to report the preparation and structures of two closely related cubane-like iron nitrosyl clusters, $Fe_4(NO)_4(\mu_3\text{-}S)_4$ and $Fe_4(NO)_4(\mu_3\text{-}S)_2(\mu_3\text{-}NC(CH_3)_3)_2$. The latter differs from the former by the presence of two triply bridging *N-tert*-butyl groups instead of two electronically equivalent, triply bridging sulfur atoms. This work was a direct consequence of our desire to assess (and thereby hopefully to differentiate) between a possible second-order Jahn-Teller effect and unusual steric effects of the *N-tert*-butyl ligands on the recently determined geometry of the cubane-like $Co_4(NO)_4(\mu_3\text{-}NC(CH_3)_3)_4$molecule[1] by the synthesis and structural

(1) R. S. Gall, N. G. Connelly, and L. F. Dahl, *J. Amer. Chem. Soc.*, **96**, 4017 (1974).