structures. We also note that this presumed coincidence must be invoked in neon, argon, and nitrogen matrix environments.

However, let us for the moment accept that there *is* an exact overlap for one of these models—the trigonal bipyramid—and proceed to calculate the isotope structure expected for the E′ and A_2'' modes. Assuming that these two stretching modes are effectively uncoupled from bends of the same symmetry, the positions of the ^{50}Cr, ^{53}Cr, and ^{54}Cr absorptions are determined solely from the appropriate **G** matrix terms, within the harmonic oscillator approximation. The relevant expressions are

$$G_{E'} = (1/M_F) + (3/2M_{Cr}) \qquad G_{A_2''} = (1/M_F) + (2/M_{Cr})$$

and as these are clearly different, one must anticipate differences in the isotope shifts for the two modes. The resulting spectrum will therefore be a superposition of two distinct isotope patterns. Figure 1c summarizes the results of our isotope calculations, and it is clear that, at the resolution of our spectrum (Figure 1a), we should observe *doublets* for the ^{50}Cr and ^{54}Cr components (separation 1.0 cm^{-1}) and a broadening of the ^{53}Cr absorption(s) if this spectrum were due to D_{3h} CrF_5.

The C_{2v} model proposed by J&W is derived from electron diffraction studies[10] and accompanies Figure 1d. It contains three independent sets of Cr–F bonds and is expected[7] to show *three* prominent IR stretches. This model thus requires the accidental overlap of *three* IR stretches to better than ca. 1.0 cm^{-1} in three different matrix environments, and is even less likely! More significantly, this structure can also be rejected on the basis of differential isotope shifts for the proposed[3] B_1 and B_2 modes. This C_{2v} model contains two pairs of equivalent CrF_2 units with interbond angles of 169.6° (axial) and 129.6° (equatorial). The Cr isotope shifts for these antisymmetric stretching modes are angle dependent, and Figure 1d shows the patterns computed by assuming an exact overlap of the ^{52}Cr B_1 and B_2 components. The outer isotopic components again appear as doublets, and this model is therefore also inconsistent with the observed spectrum. In a similar way, we are able to reject the C_{4v} structure.

We therefore believe, first, that there are no compelling grounds on which to reject the assignment of this IR spectrum to O_h CrF_6 and, more importantly, that the observed spectrum cannot be due to a CrF_5 molecule with the above D_{3h}, C_{4v}, or C_{2v} shape.

We now examine the suggestion made by Marsden and Wolynec (M&W)[4] that our spectrum could arise from molecular CrF_6 which has a trigonal-prismatic geometry, where the angle between each Cr–F bond and the C_3 axis is 50.5°. This structure also yields two IR-active stretches (E′ + A_2''), and Figure 1e shows the isotope pattern calculated by assuming an exact overlap (at 760 cm^{-1}) of the ^{52}Cr components. Once again, it turns out that we should observe *doublets* for the ^{50}Cr and ^{54}Cr components, and this model must similarly be rejected. However, since the basic prismatic structure still retains some flexibility with respect to the F–Cr–F bond angles, it is interesting to examine whether a *specific* geometry exists for which the E′ and A_2'' isotope patterns *would* be indistinguishable from those of the octahedron. For this, it is necessary that the **G** matrix terms for these two stretches should *both* be equivalent to the $G_{T_{1u}}$ stretch in O_h CrF_6. This may seem an unlikely event, but it in fact occurs when each Cr–F bond is at an angle of 54° 44′ to the C_3 axis. For this specific geometry, the observed isotope splittings could correspond to either a D_{3h} or an O_h structure, but for the prism, the assumption of band overlap in three different matrices would remain....

Finally, we note that Edwards clearly states[11] that CrF_5 vapor is *crimson* and that all the above studies have been carried out on a *yellow* vapor. J&W do not give detailed analytical figures for their product, but we believe that they may have prepared samples which are *primarily* red, less volatile CrF_5 but which contain some yellow, volatile CrF_6. Their observations on the *condensed-phase* material would thus be consistent with previous reports[12] on liquid or solid CrF_5, but their *vapor-phase* and matrix studies would be dominated by the more volatile CrF_6. In his original paper describing the synthesis of CrF_6, Glemser[1] states that the reaction between fluorine and chromium gives a mixture of *red* and *yellow* products, and we remain convinced that the yellow material is chromium hexafluoride.

Registry No. CrF_6, 13843-28-2; Cr, 7440-47-3; CrO_3, 1333-82-0; CrF_5, 14884-42-5.

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[10] Jacob, E. J.; Hedberg, L.; Hedberg, K.; Davis, H.; Gard, G. L. *J. Phys. Chem.* **1984**, *88*, 1935.

[11] Edwards, A. J. *Proc. Chem. Soc., London* **1963**, 203.

[12] See, e.g.: Brown, S. D.; Loehr, T. M.; Gard, G. L. *J. Chem. Phys.* **1976**, *64*, 260.

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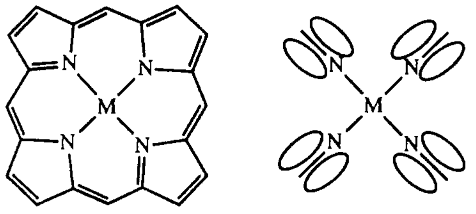
A New Class of Tetrapodal Ligands

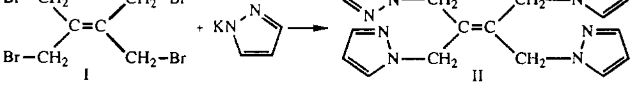
There are known large numbers of planar tetradentate and several types of tripodal ligands for metals. However, tetrapodal heterocyclic ligands seem to be unknown. In probing the reasons for the seemingly special characteristics of porphyrins, we have sought ways of preparing complexes having the four heterocyclic rings turned 90° from their positions in porphyrins, illustrated with π-orbital sketches:



Porphyrin Tetrapod

This change would allow us to test the effects of porphyrin delocalization, introduce a different kind of dpπ overlap, and perhaps provide novel biomimetic model systems. While tripod ligands are available by attaching heterocycles to a tetrahedral atom[2-4] tetrapodal ligands provide an additional problem in that a square base is needed and the lone pairs on each nitrogen would be directed toward the metal so that the four heterocycles are in parallel planes.

We approached this design using the slightly rectangular (2.8 Å × 2.7 Å) tetramethyleneethene structure to provide a square framework for the four pendant ligands. This has the advantage and/or disadvantage of possible interaction of the metal with the double bond but protection of one coordination site is assured if chelation occurs. Importantly, the syntheses are straightforward as illustrated in



As a first example, a suspension of potassium pyrazolide in tetrahydrofuran was treated with 1,4-dibromo-2,3-di(bromo-

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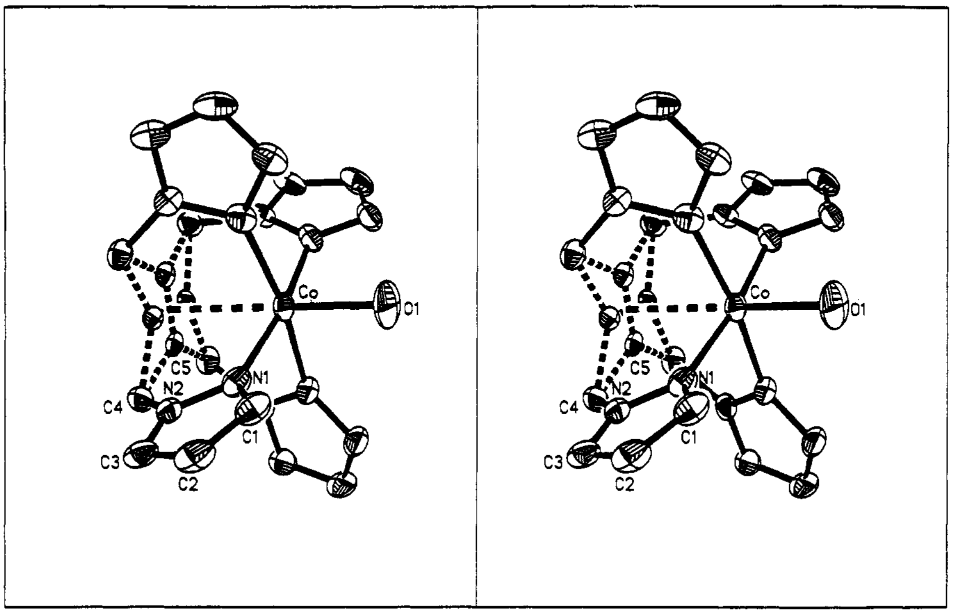

Figure 1. Stereoscopic projection of a perspective view of the crystal structure of (tetrakis(1-pyrazolylmethyl)ethene)cobalt(II) perchlorate, drawn with 20% probability ellipsoids.

methyl)-2-butene (I), prepared according to Cope and Kagan,[5] at room temperature. After potassium bromide was filtered off, followed by partial evaporation of the filtrate, the product crystallized. Recrystallization from acetone afforded a 40% yield of tetrakis(1-pyrazolylmethyl)ethene (II, TPAME): mp 145 °C; NMR δ 4.93 (s, 8 H), 6.27 (t, 4 H), 7.52 (d, 4 H), 7.56 (d, 4 H).

Combining methanolic solutions of II with methanolic solutions containing molar equivalents of copper(II), cobalt(II), iron(II), or nickel(II) perchlorates produced variously intensified colors and rapid formation of colored crystals.[6] Warming to dissolve and adding 10–20% water, followed by cooling and/or evaporation, afforded crystals suitable for X-ray crystallography.

The crystal structure of the cobalt(II) perchlorate complex is shown in Figure 1. The copper and iron complexes have the same space group and the same structure. Because of the disorder in the crystals the individual bond lengths are somewhat inaccurate.[6] The ring planes are rotated only 14° from the vertical planes. The N–Co–N angles and N–Co distances show that tetrapodal geometry has been achieved. The cobalt atom is 0.18 Å from the N_4 plane in the direction of the bound water and is 2.4 Å from the C=C plane, compared to 2.1 Å in most metal–π-bond complexes. This means that complexes of this type are very similar to five-coordinated metalloporphyrins such as chelated protoheme in that a weakly bound fifth ligand is present.[7] If electron density equal to that provided by the porphyrin dianion can be supplied, such complexes might resemble metalloporphyrins. We can use a number of heterocycles to investigate both geometry and electron density. For example, tetrapodal ligands using two imidazolide and two imidazole groups should form complexes resembling metalloporphyrins.

An additional attribute of this class of ligands is the juxtaposition of the double bond. We are curious to see how the metal–π-bond distance varies with the type and oxidation state of the metal and how these changes affect the property of the double bond. We conjecture that, using the proper CH_2–C–N angle and the appropriate metal, we will be able to vary this interaction from one in which the π bond merely protects one coordination site to one in which the alkene–metal complex is very strong. It is possible that such a π-bond is a perfectly good fifth ligand for pentadentate systems. In the present case the distance from the center of the alkene to the cobalt indicates only weak interaction with the metal. It would be interesting to study the effects of altering the electron density at the metal on its interaction with the π-bond.

The facile synthesis of this class of ligands through I or analogues of I containing other leaving groups, the ease of elaboration, and the ready formation and crystallization of the metal complexes make this new class of ligands attractive for transition-metal chemistry in general and biomimetic chemistry in particular.[7,8]

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Supplementary Material Available: Tables of atomic coordinates and equivalent isotropic thermal parameters, bond distances and bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and figures showing a perspective view of the structure and the unit cell packing diagram (6 pages); a table of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(8) Iron(III) perchlorate forms a crystalline complex with II. This complex is a catalyst for epoxidation of cyclohexene using pentafluoroiodosylbenzene as oxidant.

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A Remarkable Hypoelectronic Indium Cluster in K_8In_{11}

We have discovered that the unprecedented, electron-poor "naked" cluster anion In_{11}^{7-} exists in the binary phase K_8In_{11}, with the added feature that one electron per formula unit is apparently delocalized in a conduction band. This result provides the first homoatomic indium cluster and evidently the first example of a