Reflections on art in science

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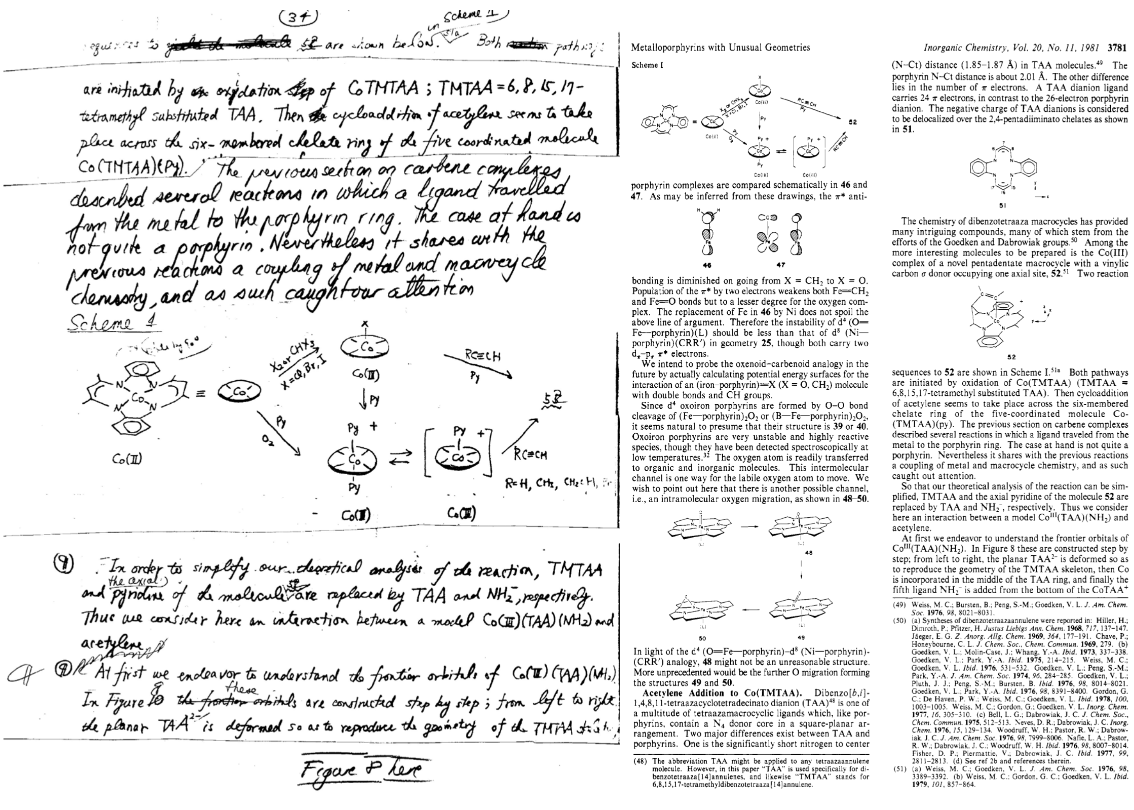
That art and science would both be part of me was clear from college days at Columbia University. The world opened up, with the help of Mark Van Doren in poetry, of Donald Keene in Japanese literature, of Howard McParlin Davis in Renaissance art. In the end I had the courage to tell my parents I didn't want to be a doctor, but not enough courage to tell them I wanted to study art history. Though it certainly wasn't obvious at the beginning, chemistry proved to be a wonderful compromise. Art, always there to be contemplated or read, then came directly into my life; in mid-life I began to write – first poetry, then essays, then plays. In time I carved out my own land 'twixt poetry, philosophy, and chemistry.

Art in science

One can see art in the elegance of, say, a simple symmetry argument for why one reaction goes one way, or another. And one can see it in more workman-like fashion in the grappling of chemists with representation of molecules. The underlying reality, of bonded atoms, begs to be communicated. The molecules are three-dimensional, the media for telling others about them a sheet of paper, a computer screen. The chemist, even if he or she today is aided by computer rendering, has to make choices of representation. Choices that he may not have been trained to craft, choices that are inherently artistic.

With no pretensions to high art, here is an example. Kaz Tatsumi and I were writing a paper about porphyrins. At left in the figure below is a true cut-and-paste manuscript, in both of our hands. Allowing you to date the paper. You can also see us struggling with the representation, deciding that the whole ring drawn had too much detail, and should be replaced by a schematic circle centered by cobalt. At right is the article as published. The drawings for it were done in India ink on tracing paper. It was the old days, as I said.


sequences to 52 are shown in Scheme I.[51a] Both pathways are initiated by oxidation of Co TMTAA; TMTAA = 6,8,15,17-tetramethyl substituted TAA. Then cycloaddition of acetylene seems to take place across the six-membered chelate ring of the five coordinated molecule Co(TMTAA)(Py). The previous section on carbene complexes described several reactions in which a ligand travelled from the metal to the porphyrin ring. The case at hand is not quite a porphyrin. Nevertheless it shares with the previous reactions a coupling of metal and macrocycle chemistry, and as such caught our attention

Scheme I

In order to simplify our theoretical analysis of the reaction, TMTAA and the axial pyridine of the molecule 52 are replaced by TAA and NH_2^-, respectively. Thus we consider here an interaction between a model Co(III)(TAA)(NH_2) and acetylene.

At first we endeavor to understand the frontier orbitals of Co(III)(TAA)(NH_2). In Figure 8 these orbitals are constructed step by step; from left to right the planar TAA^{2-} is deformed so as to reproduce the geometry of the TMTAA sk...

Figure 8 here

Metalloporphyrins with Unusual Geometries — *Inorganic Chemistry, Vol. 20, No. 11, 1981* **3781**

Scheme I

porphyrin complexes are compared schematically in **46** and **47**. As may be inferred from these drawings, the π^* antibonding is diminished on going from X = CH_2 to X = O. Population of the π^* by two electrons weakens both Fe=CH_2 and Fe=O bonds but to a lesser degree for the oxygen complex. The replacement of Fe in **46** by Ni does not spoil the above line of argument. Therefore the instability of d^4 (O=Fe—porphyrin)(L) should be less than that of d^8 (Ni—porphyrin)(CRR′) in geometry **25**, though both carry two d_π–p_π π^* electrons.

We intend to probe the oxenoid–carbenoid analogy in the future by actually calculating potential energy surfaces for the interaction of an (iron–porphyrin)=X (X = O, CH_2) molecule with double bonds and CH groups.

Since d^4 oxoiron porphyrins are formed by O–O bond cleavage of $(Fe—porphyrin)_2O_2$ or $(B—Fe—porphyrin)_2O_2$, it seems natural to presume that their structure is **39** or **40**. Oxoiron porphyrins are very unstable and highly reactive species, though they have been detected spectroscopically at low temperatures.[32] The oxygen atom is readily transferred to organic and inorganic molecules. This intermolecular channel is one way for the labile oxygen atom to move. We wish to point out here that there is another possible channel, i.e., an intramolecular oxygen migration, as shown in **48–50**.

In light of the d^4 (O=Fe—porphyrin)–d^8 (Ni—porphyrin)(CRR′) analogy, **48** might not be an unreasonable structure. More unprecedented would be the further O migration forming the structures **49** and **50**.

Acetylene Addition to Co(TMTAA). Dibenzo[*b,i*]-1,4,8,11-tetraazacyclotetradecinato dianion (TAA)[48] is one of a multitude of tetraazamacrocyclic ligands which, like porphyrins, contain a N_4 donor core in a square-planar arrangement. Two major differences exist between TAA and porphyrins. One is the significantly short nitrogen to center (N–Ct) distance (1.85–1.87 Å) in TAA molecules.[49] The porphyrin N–Ct distance is about 2.01 Å. The other difference lies in the number of π electrons. A TAA dianion ligand carries 24 π electrons, in contrast to the 26-electron porphyrin dianion. The negative charge of TAA dianions is considered to be delocalized over the 2,4-pentadiiminato chelates as shown in **51**.

The chemistry of dibenzotetraaza macrocycles has provided many intriguing compounds, many of which stem from the efforts of the Goedken and Dabrowiak groups.[50] Among the more interesting molecules to be prepared is the Co(III) complex of a novel pentadentate macrocycle with a vinylic carbon σ donor occupying one axial site, **52**.[51] Two reaction sequences to **52** are shown in Scheme I.[51a] Both pathways are initiated by oxidation of Co(TMTAA) (TMTAA = 6,8,15,17-tetramethyl substituted TAA). Then cycloaddition of acetylene seems to take place across the six-membered chelate ring of the five-coordinated molecule Co(TMTAA)(py). The previous section on carbene complexes described several reactions in which a ligand traveled from the metal to the porphyrin ring. The case at hand is not quite a porphyrin. Nevertheless it shares with the previous reactions a coupling of metal and macrocycle chemistry, and as such caught out attention.

So that our theoretical analysis of the reaction can be simplified, TMTAA and the axial pyridine of the molecule **52** are replaced by TAA and NH_2^-, respectively. Thus we consider here an interaction between a model $Co^{III}(TAA)(NH_2)$ and acetylene.

At first we endeavor to understand the frontier orbitals of $Co^{III}(TAA)(NH_2)$. In Figure 8 these are constructed step by step; from left to right, the planar TAA^{2-} is deformed so as to reproduce the geometry of the TMTAA skeleton, then Co is incorporated in the middle of the TAA ring, and finally the fifth ligand NH_2^- is added from the bottom of the $CoTAA^+$

(48) The abbreviation TAA might be applied to any tetraazaannulene molecule. However, in this paper "TAA" is used specifically for dibenzotetraaza[14]annulenes, and likewise "TMTAA" stands for 6,8,15,17-tetramethyldibenzotetraaza[14]annulene.

(49) Weiss, M. C.; Bursten, B.; Peng, S.-M.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 8021–8031.
(50) (a) Syntheses of dibenzotetraazaannulene were reported in: Hiller, H.; Dimroth, P.; Pfitzer, H. *Justus Liebigs Ann. Chem.* **1968**, *717*, 137–147. Jäger, E. G. *Z. Anorg. Allg. Chem.* **1969**, *364*, 177–191. Chave, P.; Honeybourne, C. L. *J. Chem. Soc., Chem. Commun.* **1969**, 279. (b) Goedken, V. L.; Molin-Case, J.; Whang, Y.-A. *Ibid.* **1973**, 337–338. Goedken, V. L.; Park, Y.-A. *Ibid.* **1975**, 214–215. Weiss, M. C.; Goedken, V. L. *Ibid.* **1976**, 531–532. Goedken, V. L.; Peng, S.-M.; Park, Y.-A. *J. Am. Chem. Soc.* **1974**, *96*, 284–285. Goedken, V. L.; Pluth, J. J.; Peng, S.-M.; Bursten, B. *Ibid.* **1976**, *98*, 8014–8021. Goedken, V. L.; Park, Y.-A. *Ibid.* **1976**, *98*, 8391–8400. Gordon, G. C.; De Haven, P. W.; Weiss, M. C.; Goedken, V. L. *Ibid.* **1978**, *100*, 1003–1005. Weiss, M. C.; Gordon, G.; Goedken, V. L. *Inorg. Chem.* **1977**, *16*, 305–310. (c) Bell, L. G.; Dabrowiak, J. C. *J. Chem. Soc., Chem. Commun.* **1975**, 512–513. Neves, D. R.; Dabrowiak, J. C. *Inorg. Chem.* **1976**, *15*, 129–134. Woodruff, W. H.; Pastor, R. W.; Dabrowiak, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 7999–8006. Nafie, L. A.; Pastor, R. W.; Dabrowiak, J. C.; Woodruff, W. H. *Ibid.* **1976**, *98*, 8007–8014. Fisher, D. P.; Piermattie, V.; Dabrowiak, J. C. *Ibid.* **1977**, *99*, 2811–2813. (d) See ref 2b and references therein.
(51) (a) Weiss, M. C.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 3389–3392. (b) Weiss, M. C.; Gordon, G. C.; Goedken, V. L. *Ibid.* **1979**, *101*, 857–864.

My claim is that the chemical structures that adorn the 21,000+ per year pages of the *Journal of the American Chemical Society* (in as high density of illustrations as you see above) are art as well as science — not great art, but art nevertheless. Even if their creators are unaware that they

are producing art, even if they would deny the act, the “conceit” of being artists (revealing thereby an interesting ambiguity toward art), what they are doing is the following: From a certain reality, that of a molecular model (which, like all realities, turns out to be on close examination a representation of a representation of . . .), the creators of these drawings try as hard as they can to abstract the essence. Then they attempt to communicate that essence to others, using a certain visual vocabulary. There is a concentration in what they do, an intensity that makes the object marked for communication come to life. Interestingly, there is also a distancing from the object (it’s rendered from outside; it is remote) and a drawing in. Significant formal considerations — the relationship of the parts of a molecule to its whole — are essential.

An argument can be made that what is missing is (a) the chance, therefore unique, aspect of artistic creation, and (b) the affective realm, the play of the emotions, in this process of communication. To expand on the first point, which I think has some merit (see also my “Abstract Science?” American Scientist, **97**, 450-453 (2009)): while an artist’s oeuvre reveals similarities, each work is different, a varied creation. The aleatory aspect, capitalized upon, is central. Scientific representations aspire, on the other hand, if not to anonymity, then to perfect paraphrase. All those chemists who wind up drawing slightly different structures want other chemists to see the same molecule. And they do, by and large, see the underlying shared structure.

I will not argue too strongly with that. However, it has been my personal experience that, despite the assumed intent of perfect paraphrasability, the creative moment in chemistry derives from a perception (often spatial) of a molecule in just one way and not another.

We see that in the work of great synthetic chemists, master makers of molecules. The model turned in the hand in just one way, a redrawing of a structure with a certain unrealistic distortion, allowed them—and only them—to see it in a certain manner, to take it apart in the process of finding a startling way to put it together.

As for the emotional realm—well, I would agree that it is suppressed in the prescribed discourse of scientists. But first of all, to those privy to the code, that little free-floating picture can have tremendous emotional impact: something novel, something beautiful, a challenge to make, envy of the maker.

Second, we have learned from literature and Freud what the consequences of suppression are. Here is a creative activity of human beings — science. Deep down it is driven by the same complex mix of psychic motives that drive any creation. The id will out. But the people who are doing this creative activity claim to be just reporting the facts and nothing but the facts. At best they may be fooling themselves, for the facts are mute. The very same impersonal, neutered language in which they choose to express themselves becomes charged with rhetorical impulses, claims to power, all the things they (we) foolishly thought we could suppress.

Poetry

From visual art, I came above to language. A special form of writing, poetry, has been important to me all my life. Not that I would be foolish enough to write my science in verse; I need to get it by the gatekeepers, and we know how they would savage a poem. No, my subversions are tiny: For instance I sneaked in the title of a recent paper in… the *Proceedings of the National Academy of Sciences* “A Little Bit of Lithium Does a Lot for

Hydrogen." And in the *Journal of the American Chemical Society*, another recent article of ours bore the title, "(Barely) Solid $Li(NH_3)_4$" What a small victory it was to be allowed to begin a title with a word in parentheses! And you are right to damn the victory as that of cuteness rather than poetry.

There are other strategies I use to gain the slightest emotional edge. For if in talking of dry molecular orbitals I can somehow, through a word or two, get the graduate student reader to feel that it is a human being who is speaking to them, and that, moreover, I care that they understand, then I have them. They will read that paper; that tiny emotional contact in a sea of "optimized energies", "density functional calculations" and worse, touches people.

But actually there is a poetic element in my science. My métier is theoretical chemistry — obtaining quantum mechanical knowledge of where electrons are in molecules, and extracting from that knowledge rationalizations, trends, and predictions of the shapes and reactivities of molecules. The poetry, comfortably ensconced in the cognitive framework of chemistry, is in shaping concise, portable, perhaps elegant explanations. Hard won, it's in the drawing of unexpected connections (so close to metaphor!) between things that at first sight might seem unconnected. An example, making sense to chemists, is the similarity, not identity, I proposed of the disposition of electrons in the very organic methyl radical (CH_3) and the very inorganic trisphosphinocobalt fragment ($Co(PH_3)_3$). Surprise, economy of statement, structures of similarity and difference— these are the poetic elements in my science.

When I began to write poetry I had naive notions that I could talk of science, maybe teach it, in poetry. Science eventually entered my poetry

but in other ways. First there was the language of science—a natural language under stress, therefore inherently poetic. Under stress, because science is continually forced to express new things with the same old words. And to define things in words that refuse to be unambiguous. I spot found poems in this language of science.

I also began to see metaphor, for free, and floating all around in science. Just like Samuel Taylor Coleridge, who said that when he was in want of metaphor, he went to a lecture of Humphry Davy. Reaching a balance where that metaphor was not used gratuitously, but had meaning both within science and as poetry—that hasn't been easy.

Here is a poem of mine in which science figures:

Quantum Mechanics

Beginnings
are always
classical.
It's chemis-
try after
all – to burn
a log needs
to be near
another.

It's at its
most spooky
while growing.
What one may
see, so does
the other;
there being

no evi-
dence entan-
glement falls
off with sep-
aration.

Mature, it
isn't fazed
by singu-
larities,
a theory
that can ac-
comodate
boundary
tensions.

And how will
it end? Like
a love, in
a world de-
monstrably
false, in the
vacuum,
its place filled
by the new.

My problem in this poem was to say reasonable things about the evolution of quantum mechanics in the 20th century, while getting away with something no serious quantum mechanic would dream of doing—seeing the parallel to a love. But…withholding, if I could, the realization in the

reader of that parallel being drawn (hey, drawing parallels is a scientistic metaphor!) until the poem was near its end.

In my mind, the poem began with reading in *Physical Review Letters* of some recent experiments, related to Schrödinger's Cat arguments, that seemingly showed that entanglement (cat dead, cat alive) did not fall off with distance. Isn't that a poem by itself? Do we need more proof of the natural connection of science and poetry?

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