accomplished by grinding the disastereoisomers with cold, concentrated hydrobromic acid which contained a little water. A sample of *d*-$[Cr(en)_2(C_2O_4)][CoC_{10}H_{12}N_2O_8]\cdot H_2O$ which weighed 0.275 g (0.00044 mole) was ground at 0° with a solution which contained 0.75 ml of concentrated hydrobromic acid and 0.4 ml of water. After 10 min of grinding, the orange crystals of *d*-$[Cr(en)_2(C_2O_4)]Br\cdot H_2O$ were collected by filtration and washed with cold, concentrated hydrobromic acid until the filtrate turned from the deep purple of the cobalt complex to a pale orange. Any excess acid was removed by washing with cold alcohol, followed by acetone and ether. This procedure gave 0.141 g (71% based on the racemate) of a pale orange powder. The specific rotations of a 0.1% solution at the sodium D line and at 5461 A were +275 and +510°, respectively.

The *d* form was suspended in a small amount of ice-cold water and ground for 10 min to remove any racemate present. After two such treatments, the specific rotations of a 0.1% solution at the D line and 5461 A were constant at +310 and +600°, respectively. The yield of this isomer was 0.120 g (60% based on the racemate). *Anal.* Calcd for *d*-$[Cr(en)_2(C_2O_4)]Br\cdot H_2O$: Cr, 14.5; C, 20.12; Br, 22.3. Found: Cr, 14.9; C, 20.38; Br, 22.5.

The *l* diastereoisomer was treated as described above and gave 0.090 g (45% based on the racemic complex) of a pale orange powder. The specific rotations of a 0.1% solution at the D line and 5461 A were −305 and −625° after two grindings with cold water. *Anal.* Calcd for *l*-$[Cr(en)_2(C_2O_4)]Br\cdot H_2O$: Cr, 14.5; C, 20.12; Br, 22.3. Found: Cr, 14.7; C, 20.38; Br, 22.5.

The resolution works equally well using *d*-$K[CoC_{10}H_{12}N_2O_8]\cdot 2H_2O$ as the resolving agent. However, in this case, the fraction which precipitated at 25° contained the *l* isomer and the fraction obtained at 0° contained the *d* isomer.

Analytical Methods and Instrumentation.—Chromium was determined by oxidation to dichromate with hot perchloric acid followed by titration with a standard iron(II) solution to the ferroin end point. All microanalyses were performed by the Spang Micro Analytical Laboratory, Ann Arbor, Mich. Optical rotations were taken on a Bendix–Ericsson Type 143-A ETL-NPL automatic polarimeter. Appropriate glass filters were used to isolate the desired wavelengths, and all measurements were at room temperature. Syringe-type cells with 40-mm path lengths were used.

Discussion

A new method has been developed for the resolution of the oxalatobis(ethylenediamine)chromium(III) ion. The molar rotations are in agreement with those reported by Werner and Bosshart[2] (literature[2] values, $[M]_{\mathrm{D}}$ +1129° and $[M]_{\mathrm{L}}$ −1075°; this work $[M]_{\mathrm{D}}$ +1110° and $[M]_{\mathrm{L}}$ −1090°) and about 180° higher than the value given by Bushra and Johnson.[4]

Correspondence

A Solution to the Structural Dilemma of $Co_4(CO)_{12}$ Based on Valence Tautomerism and Steric Nonrigidity[1]

Sir:

The problem of the structure of tetracobalt dodecacarbonyl, $Co_4(CO)_{12}$, presents an interesting and significant challenge on the basis of the information available in the literature. Corradini[2] studied the structure of the crystalline substance using zonal data with the following results. (1) There is an approximately regular tetrahedron of cobalt atoms. (2) The molecules are disordered making it impossible, with the data available to him, to specify directly and conclusively the arrangement of the CO groups. (3) The most likely arrangement of CO groups *for the molecule in the crystal* is one in which one Co atom is bound to three terminal CO groups while the other three Co atoms are each bound to two terminal CO groups with the three edges between them being spanned by bridging CO groups. This structure possesses idealized C_{3v} symmetry.

The infrared spectrum measured in pentane solution under fairly high resolution[3] contained only four well-defined peaks in the terminal CO-stretching region and one in the bridging region, whereas the C_{3v} structure should have six and two bands in these regions, respectively. It was pointed out[3] that the discrepancy is surprising but that the spectrum is not *necessarily* inconsistent with Corradini's structure. It may be noted here, however, that the extent to which accidental degeneracies and/or extreme weakness of CO-stretching bands must be assumed in order to correlate the infrared data with the C_{3v} structure is disquieting.

More recently, Smith[4] showed that a structure containing the Co_4 tetrahedron with four bridging groups and two terminal groups on each Co atom so arranged as to give D_{2d} symmetry should have precisely the infrared spectrum observed in solution, and he therefore questioned the correctness of Corradini's structure. Quite recently, Corradini[5] has tested Smith's structure against his crystallographic data and considers that it is inadmissible *in the crystal*.

The purpose of this communication is to point out that Corradini's work and Smith's work are not necessarily incompatible and to suggest some ideas which can resolve the apparent inconsistency and which have some further implications.

As the very first step, it should be noted that the infrared data and the X-ray crystallographic data pertain to two different phases and that the structure does not have to be the same in both.[6]

[1] The substance of this correspondence and explicitly the summary statements were part of a lecture presented on Feb 3, 1966, at the Middle Atlantic Regional Meeting of the American Chemical Society, Philadelphia, Pa.

[2] P. Corradini, *J. Chem. Phys.*, **31**, 1676 (1959).

[3] F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 1882 (1960).

[4] D. L. Smith, *J. Chem. Phys.*, **42**, 1460 (1965).

[5] P. Corradini, private communication.

[6] There are a great many examples of this variability of structure with phase throughout chemistry. Two which are particularly close to the present one are those of $Fe_3(CO)_{12}$ and $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2$, both of which have infrared spectra in solution which are quite inconsistent with the structures of the molecules in the solid state and which thus indicate the presence of molecules with different structures in solution.

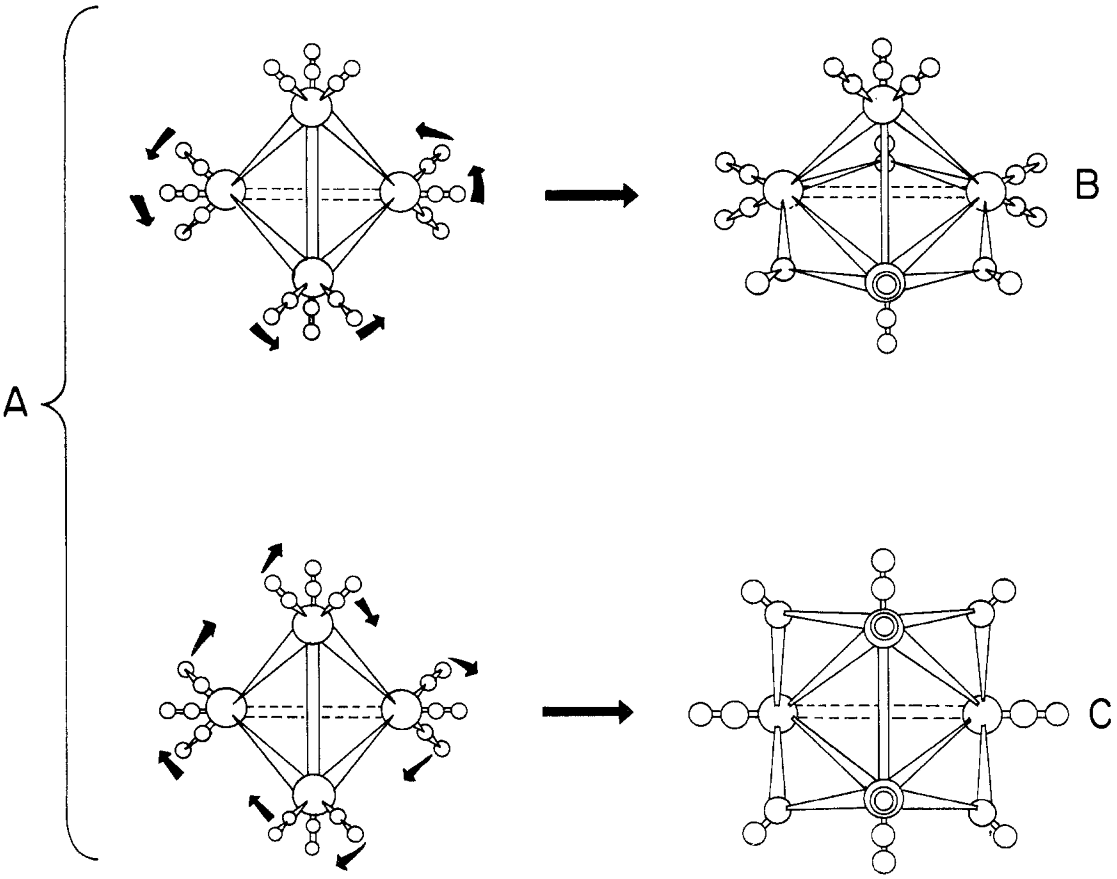


Figure 1.

The gist of the idea proposed here is expressed in Figure 1. Structure A is one without bridging CO groups. It has T_d symmetry and is closely related (*vide infra*) to a cuboctahedron. There is no evidence for this as an observable structure for $Co_4(CO)_{12}$. Structure B is Corradini's; structure C is Smith's. It is seen that A can be transformed intramolecularly into either B or C by small quasi-rotatory shifts of some CO groups. These shifts and the structures they interrelate represent a kind of valence tautomerism, in which each CO group can maintain an attachment to the Co atom to which it is initially attached in A during one cycle of transformation.

Conversely, B and C can each be transformed into A and when the B → A, A → B and C → A, A → C shifts are repeated often enough in different but equivalent ways, the nonequivalent CO groups of B and C are completely permuted and exchanged. Moreover, assuming that Smith's structure is the correct one in solution, the pathway B → A → C provides a seemingly facile path for the structural change.

Closer examination of structures A, B, and C reveals some significant facts. Suppose we begin with A and allow one CO on one Co atom ($Co^{(1)}$) to reach across one of the three edges of the Co_4 tetrahedron accessible to it, to form a bridge. Without loss of generality, we may call this the $Co^{(1)}$–$Co^{(2)}$ edge. $Co^{(1)}$ is now short one electron and $Co^{(2)}$ has an excess electron. This would appear to be an unstable situation, and the next step (aside from a reversal of the step just taken) would be for a CO group on $Co^{(2)}$ to reach across to one of the two neighboring Co atoms not yet bridged. The two choices yield equivalent results, and we may call the one selected $Co^{(3)}$. Now $Co^{(3)}$ will have the excess electron, and one of its terminal CO groups may brachiate to a neighboring Co atom. Again there are two choices, but now the two paths give different results. If it reaches over to $Co^{(1)}$, all Co atoms have acceptable electron populations and we have, of course, Corradini's structure. If, instead, the next bridge is swung from $Co^{(3)}$ to $Co^{(4)}$ then $Co^{(4)}$ is overpopulated and one of its terminal CO's will swing to $Co^{(1)}$ giving Smith's structure. The purpose of considering this line of reasoning is not to propose that such stepwise sequences necessarily occur rather than concerted A $\rightleftharpoons$ B or A $\rightleftharpoons$ C shifts but to demonstrate that B and C are the only two edge-bridged structures with no more than one bridge per edge which are possible (in the sense of not offending simple and generally accepted rules for valence and electron counting in such compounds).[7]

Structure A is an intrinsically reasonable one and should not be particularly unstable in an absolute sense.[8]

---

(7) Of course, other structures could be considered in which more than two bridges per edge or triple bridges on the faces are permitted but all have very low symmetry. Even the one with four face bridges and no edge bridges, which might be considered in analogy to the structure implied for $[(\pi\text{-}C_5H_5)FeCO]_4$ by the single CO absorption band reported for it (*cf.* R. B. King, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 22-O), has at best C_s symmetry.

(8) This says nothing, of course, as to its stability *relative* to other reasonable structures such as B and C, for $Co_4(CO)_{12}$, but is a necessary condition for it to be considered as an intermediate accessible from the others at ambient temperature, even though less stable than the others.

The bonding may be seen to be satisfactory by a simple valence-bond analysis in which the nine valence shell orbitals of each metal atom are divided into three sets. Three empty trigonally directed (hybrid) orbitals are used for σ bonds to the CO groups. Three more filled orbitals are used mainly for π donation to the CO groups. This leaves three half-filled trigonal orbitals directed approximately toward the neighboring three CO atoms. The entire set of 12 such orbitals and 12 electrons suffices to form six two-electron Co–Co bonds and six empty Co–Co antibonding orbitals. An equivalent MO formulation[9] in which the electronic configuration is $(A_1)^2(E)^2(T_2)^2(T_1^*)(T_2^*)$ or $(A_1)^2(T_2)^2(E)^2(T_1^*)(T_2^*)$ (where the asterisk denotes an antibonding orbital) has also been developed.[10]

To summmarize and extend into the realm of prediction (something which a pragmatically valid idea should be capable of) the foregoing ideas, the following specific statements are made.

(1) Two reasonable molecular structures containing bridges are possible and interconvertable by the mechanism suggested here. These are the only ones of the type in which there are only singly bridging CO groups (so-called "ketonic" bridges) and no more than one such bridge on any edge of the Co_4 tetrahedron.

(2) It is thus quite possible and indeed likely (though *not* certain) that both Smith and Corradini are correct—each for the phase with which he was dealing.[10a]

(3) There is considerable likelihood that if either or both of the rearrangement processes considered, *i.e.*, $A \rightleftharpoons B$, $A \rightleftharpoons C$, are sufficiently fast, all CO groups will appear nmr equivalent (using ^{13}C or ^{17}O) even though they are not in either of the structures B or C.[10–12]

(4) The opportunity for facile internal rearrangement is even greater than that implied by the $A \rightleftharpoons B$, $A \rightleftharpoons C$ paths. The close resemblance of the arrangement of the CO groups in structure A to the arrangement of the 12 vertices of a cuboctahedron leads to the following idea. The Co atoms can be thought of as instantaneously lying inside one set of four triangular faces of the cuboctahedron, leaving another unoccupied, tetrahedrally disposed set of triangular faces. There are then three twofold axes about which the Co_4 tetrahedron may rotate to bring it into the alternative orientation. Should such a process actually occur, it would constitute a case of valence tautomerism or steric nonrigidity quite as remarkable in its scale as that provided by Bullvalene.[13]

(5) While the structure of T_d symmetry which has no bridging groups has not been observed for $Co_4(CO)_{12}$, the general trend[14] toward lower stability of CO-bridged, M–M-bonded pairs of metal atoms as compared to unbridged pairs, as one goes from carbonyl-type compounds of the first transition series to their analogs in the second and third series, leads to a structural prediction, namely, that just possibly $Rh_4(CO)_{12}$, but much more probably $Ir_4(CO)_{12}$, may have structure A in the crystal, in solution, or in both.

Postscript.—In the discussion following the presentation of this material at the Middle Atlantic Regional Meeting of the American Chemical Society, Professor L. F. Dahl announced (a) that Dr. C. H. Wei and he have conclusively ascertained Corradini's structure for crystalline $Co_4(CO)_{12}$ by three-dimensional work, (b) that $Rh_4(CO)_{12}$ seems likely to have the same structure, but (c) that $Ir_4(CO)_{12}$ has structure A. It will be interesting to see how well the other predictions offered here stand up to experimental test.

---

[9] F. A. Cotton, unpublished work.

[10] The possibility of $B \rightleftharpoons C$ interconversion which bypasses A and instead involves a structure with just the $Co^{(1)}–Co^{(2)}$ and $Co^{(2)}–Co^{(3)}$ bridges is relatively unattractive since (1) a sequential shifting seems less likely than a concerted shift and (2) this intermediate would appear to be much less stable than A.

[10a] NOTE ADDED IN PROOF.—The author has been informed by Professor R. K. Sheline, Department of Chemistry, Florida State University, that measurements of the Co^{59} nmr spectrum of $Co_4(CO)_{12}$ in *n*-hexane solution (H. Haas, Ph.D. Thesis, Florida State University, 1965) show two closely spaced absorptions in an intensity ratio of about 3:1. If the ratio is truly 3:1, this result is most naturally explained by postulating that Corradini's structure is present in solution. Assumptions as to the weakness or overlap of CO stretching bands must then be made. It would then also be necessary to assume that neither structure A nor structure C is stable enough to persist in appreciable concentration in solution. However, the suggested intramolecular exchange of CO environments *via* structure A remains valid.

[11] The exchange of CO with $Co_4(CO)_{12}$ has already been studied[12] in benzene at 25° with the conclusion that all CO groups in the molecule exchange at the same rate. Such a result is, of course, an obvious corollary to point 3. However, in view of the ideas presented here, the dissociative mechanism previously suggested[12] is considered unnecessary and unlikely.

[12] D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).

[13] W. von E. Doering and W. R. Roth, *Angew. Chem.*, **75**, 27 (1963); *Tetrahedron*, **19**, 715 (1963).

[14] To be discussed in detail in a future publication with G. Yagupsky, but certainly apparent to those familiar with the field.

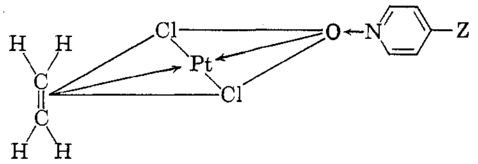
DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS 02139
F. A. COTTON

RECEIVED FEBRUARY 16, 1966

On the Interpretation of the Nuclear Magnetic Resonance Data of Kaplan and Orchin for Platinum–Olefin Complexes

Sir:

Kaplan and Orchin have recently shown[1] that in complexes of type I electron-withdrawing groups Z decrease the shielding of the ethylene protons. This is the result expected (as Kaplan and Orchin point out) from a decrease of platinum–ethylene back-bonding.



I

A more surprising result is that electron-withdrawing groups increase the coupling between the Pt^{195} and the H^1 nuclei. Kaplan and Orchin rationalize this finding by postulating a variation in the $Pt–C_2H_4$ bond length. There is, we believe, a simpler explanation.

The π^* orbitals of C_2H_4, into which the metal do-

---

[1] P. D. Kaplan and M. Orchin, *Inorg. Chem.*, **4**, 1393 (1965).