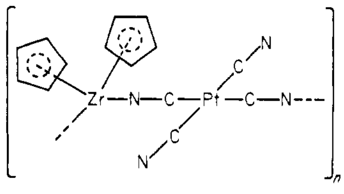
2144-cm^{-1} band is assigned to a terminal C-N stretch (B_{2u}) whose shift to higher frequency relative to $Pt(CN)_4{}^{2-}$ is attributed to a slight decrease in the π back-bonding to the CN ligand from the Pt atom. If the bridging CN ligands were cis, the local symmetry about Pt would be C_{2v} and four ν(CN) modes would be expected in the infrared and they would be coincident with the Raman bands, neither of which is true for A. Similarly, overall D_{2h} symmetry for a cyclic dimer would lead to eight IR-active ν(CN) (presumably four sets of double accidentally degenerate ones), and this is not observed. The shift in δ(C-H) from 811 to 823 cm^{-1}, together with other cyclopentadiene features, shows retention of π bonding between the cyclopentadiene and Zr and the increase in positive charge density on Zr. The 350-650-cm^{-1} region contains six bands including the ν(Pt-C) and ν(Zr-N) modes expected for the polymeric structure proposed below. In particular, the Zr-N stretch is observed at 510 cm^{-1}. The ν(Zr-I) bands of $(\eta^5\text{-}C_5H_5)_2ZrI_2$ are absent from the spectrum of A.

The Raman spectrum of $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4]_n$ contains the features expected for a cyanide-bridged species containing both the zirconocene and terminal cyanide-containing platinum moieties. There are no Raman bands of any of the homologs that clearly would be assigned to metal-metal bond stretches.

X-ray diffraction experiments on the product powders showed diffuse scattering characteristic of amorphous materials. Magnetic susceptibility measurements showed them to be diamagnetic. Due to their insolubility in common solvents, and their involatility, their molecular weights could not be determined.

On the basis of the observed properties, we propose the structure of A, in which the tetrahedral coordination about Zr and the square-planar coordination about Pt are retained. Analogous structures are proposed for $[(\eta^5\text{-}C_5H_5)_2ZrPd(CN)_4]_n$, $[(\eta^5\text{-}C_5H_5)_2HfPt(CN)_4]_n$, and $[(\eta^5\text{-}C_5H_5)_2HfPd(CN)_4]_n$.



A

The compounds synthesized possess features which present interesting chemical possibilities. For example, since the Pt (or Pd) is in the II state formally, it is a site for oxidative addition,[9] and it is feasible that ligands added in this way could be substituted for by a metal-containing nucleophile to give branched, and perhaps cross-linked, metal-containing polymers. Alternatively, such oxidative addition at M′ could weaken the CN-M interaction enough to permit weak nucleophiles, which normally could not compete effectively for M sites, to form compounds with the 4B metals. In addition, the presence of the two coordinatively and electronically unsaturated metals in these compounds may lend them catalytic activity, and this possibility is under investigation.

Acknowledgment. The support of the Materials Science Program of Brown University, sponsored by the National Science Foundation, is gratefully acknowledged. We are grateful to Ms. June Passaretti, Dr. Richard Collins, and Professor Aaron Wold of the Chemistry Department and the M.R.L. Materials Preparation Facility for assistance in obtaining the X-ray and magnetic data.

Registry No. $[(\eta^5\text{-}C_5H_5)_2ZrPt(CN)_4]_n$, 78891-74-4; $[(\eta^5\text{-}C_5H_5)_2ZrPd(CN)_4]_n$, 78891-72-2; $[(\eta^5\text{-}C_5H_5)_2HfPt(CN)_4]_n$, 78891-70-0; $[(\eta^5\text{-}C_5H_5)_2HfPd(CN)_4]_n$, 78891-68-6; $(\eta^5\text{-}C_5H_5)_2ZrI_2$, 1298-41-5; $(\eta^5\text{-}C_5H_5)_2HfI_2$, 37260-85-8; $[(n\text{-}C_4H_9)_4N]_2Pt(CN)_4$, 21518-40-1; $[(n\text{-}C_4H_9)_4N]_2Pd(CN)_4$, 21518-39-8.

Correspondence

Alterdentate Ligands

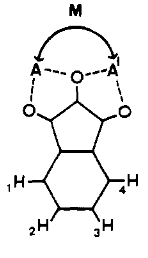
Sir:

In coordination chemistry, ligands have been classified according to various criteria. One obvious classification concerns the *denticity* of a ligand and, consequently, sequestring agents are called *unidentate*, *bidentate*, etc.[1] Another widly accepted designation is *ambidentate*,[2] which means that a ligand can coordinate through *different* ligand atoms as, e.g., nitrogen and sulfur in the thiocyanate NCS^- ion. Is the azide ion NNN^- ambidentate too?

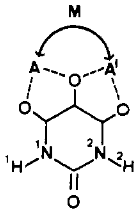
In the present paper we want to propose a designation for a class of ligands, which can form metal complexes that can undergo some well-defined modes of rearrangements.

We define as an *alterdentate ligand* a species which offers to a metal ion more than one *equivalent* coordination site. In an alterdentate ligand there is, principally, always a rearrangement possible in which the metal is transferred from one site to another one. This can be either an inter- or intramolecular process. The rearrangement reaction is kinetically controlled by the activation energy and entropy experienced by the metal on the reaction path. The free energy difference is zero by definition, if the coordination sites are equivalent.

Examples for such alterdentate ligands are found in the recently reported complexes of ninhydrine (I) or alloxan (II)



nin$^-$ (I)



all$^-$(II)

radical anions.[3] In both cases, A and A′ are equivalent coordination sites and, consequently, $\Delta G° = 0$ for (1) and (2).

$$M(A)(nin^-) \rightleftarrows M(A')(nin^-) \qquad (1)$$

$$M(A)(all^-) \rightleftarrows M(A')(all^-) \qquad (2)$$

The exchange between A and A′ can be observed by ESR spectroscopy because the spin densities at the positions H(1) to (4) in nin$^-$ and (HN)(1)/(HN)(2) in all$^-$ are modulated

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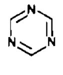
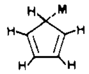
[3] Schaller, D.; von Zelewsky, A. *J. Chem. Soc., Chem. Commun.* **1979**, 948.

with the frequency of the exchange of the metal ion between sites A and A′.

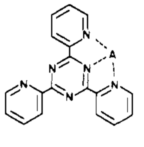
In order to make the concept as clear as possible, we want to extend the designation and we define the following subclasses: *Isoalterdentate ligands* can bind a metal ion at two or more symmetrically equivalent positions. If one of the sites is occupied, the others are still available for coordination. The number of sites can be included as a prefix. Nin$^-$ (I) and all$^-$ (II) are accordingly diisoalterdentate ligands. Sometimes, it depends on the nature of the metal ion whether a ligand acts as a *chelate* or as an *alterdentate*. In most cases en is a chelate, whereas for Ag^+ it is an alterdentate in the complex $Ag(en)_2^+$, owing to the linear coordination of the silver ion.[4] *S*-Triazine (III) is triisoalterdentate, and the cyclopentadienyl anion (IV) is pentaisoalterdentate in some (η^1-C_5H_5)M species.


(III)

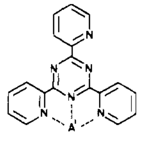


(IV)

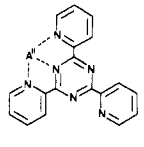
There is another type of ligand, exemplified by TPTZ (V),



(Va)



(Vb)

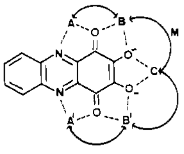


(Vc)

which can offer equivalent coordination sites. The metal can change from A to A′ to A″ (Va to Vc) only if the ligand itself rearranges simultaneously, however, and the same type of coordination sites is no longer available if one metal is bound. This class is called *anisoalterdentate*, and TPTZ is therefore trianisoalterdentate. $\Delta G°$ for the rearrangement is still 0.

Ambidentate ligands offer nonequivalent coordination sites to the metal, and, generally, $\Delta G° \neq 0$ for the exchange between sites. Of the three different isotopic species $^{15}N^{14}N^{14}N^-$, $^{14}N^{15}N^{14}N^-$, and $^{14}N^{14}N^{14}N^-$, having natural abundances of 0.74%, 0.37%, and 98.89%, the first is ambidentate and the second and the third are isoalterdentate.

The two types can be combined and the phenazine (VI)



(VI)

derivative with five sites AA′BB′C, of which AA′ and BB′ are pairwise equivalent, can be disignated as isoalterambidentate.

The proposed classification scheme emphasizes a possible nonrigidity in metal complexes, which has not been very often considered, so far, in coordination chemistry. Many alterdentate ligands are known, and many more could be designed. Experimental observation of rearrangements will, in most cases, be possible by NMR spectroscopy with diamagnetic ligands or with ESR in the case of radical ligands if the metals are sufficiently labile. For substitution-inert complexes, other methods such as isotopic labelling might be used.

Complicated polyfunctional ligands in biochemical systems could, in principal, exchange metal ions between several equivalent coordination sites, and alterdenticity may play an important role in some bioinorganic reactions, including the transport of metal ions over considerable distances.

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The Complexities of Ascorbate as a Reducing Agent

Sir:

Aqueous solutions of ascorbic acid (H_2A, vitamin C) have been widely used by inorganic chemists because of the convenience of ascorbate as a reducing agent.[1-3] We have recently utilized this reductant as a source of reducing equivalents in a multicomponent system that promotes the photoreduction of water.[4] In connection with this work information on the redox characteristics of the various species generated in the oxidation of ascorbate in water was sought. Here a summary of these findings is presented.

The structures I, II, and V shown in Figure 1 are generally given[5] for ascorbic acid, ascorbate ion (HA^-), and dehydroascorbic acid (A), respectively, but it has recently been established that VI is actually that appropriate to dehydroascorbic acid in aqueous solutions.[6] On the basis of EPR results Schuler and co-workers[7] have concluded that IV is the structure of ascorbate radical ($A^-\cdot$), the one-electron oxidation product of ascorbic acid or of ascorbate ion; its structure is invariant in the pH range 0–13, but at lower pH, $A^-\cdot$ protonates to give III.[7]

Ascorbic acid is a weak acid,[8] while the radical HA· is a very strong acid.[7] Observations by Ball suggest that dehydroascorbic acid undergoes proton loss with a pK_a of ~8.[9] Data relevant to the various protonation equilibria are summarized in Table I.

Thermodynamic data bearing on redox equilibria between the various species come from several sources. By recourse to mediators Ball performed potentiometric measurements on the ascorbic acid/dehydroascorbic acid couple (eq 1) in

$$A + 2H^+ + 2e^- = H_2A \qquad (1)$$

aqueous solutions ranging from pH 1 to 8.57 at 30 °C.[9] The reduction potential for the couple was determined to be +0.39 V in 1 N acid at 30 °C.[9] The A/H_2A couple was found to be chemically reversible in a practical sense up to about pH 7; above pH 7, the decomposition of the oxidized form became rapid, with the half-life for its decomposition decreasing from ~40 min at pH 6.7 to ~0.5 min at pH 8.6. Foerster, Weis, and Staudinger[10] used an ESR method to evaluate the con-

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