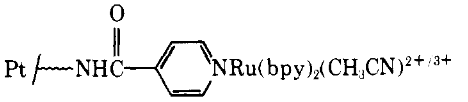
lution results in the appearance of the immobilized $RuNO^{3+/2+}$ wave. When the same electrode is exposed to a basic solution (lutidine-acetonitrile), the original $RuNO_2$ electrochemistry is regenerated, although slowly.

The third kind of immobilized complex reactivity is potentially the most significant since it relates to modified electrode electrocatalytic behavior. In solution, $[(bpy)_2Ru^{III}(py)NO_2]^{2+}$ has been shown[3] to act as a catalytic oxygen atom-transfer reagent toward triphenylphosphine to produce the corresponding phosphine oxide (Scheme II). The catalytic cycle shown can be driven electrochemically. The immobilized complex II shows similar catalytic properties. Figure 2 shows a cyclic voltammogram of I in the presence of tris(*p*-chlorophenyl)phosphine, in which the only observable[8] species remaining following a single oxidative potential sweep through the $Ru^{II}NO_2$ wave is the nitrosyl complex ($E°' = +0.50$ vs. SSCE). Since the yield of immobilized nitrosyl complex is nearly quantitative and little if any nitrato complex product is observable, the critical oxygen atom-transfer step on the chemically modified electrode surface competes effectively with the ligand oxidation steps in Scheme I. The direct electrode oxidation of $(p\text{-}ClC_6H_4)_3P$ on Pt in acetonitrile occurs at $E_{peak} = +1.49$ V vs. SSCE so that Figure 2 represents a catalytic shift in the phosphine electrolysis potential of 0.40 V.

Although the nitrosyl → nitro regeneration step is slow, the catalytic cycle suggested in Scheme II can be duplicated on the electrode surface. Catalytic currents are sustained upon phosphine, acetate ion, and trace amounts of water. There is the added complication, however, of solvolysis of II to give the acetonitrile complex[1e] c so that the catalysis is not persistent.



c

These results show that general forms of reactivity observed in homogeneous solution are reproducible, at least in qualitative detail for immobilized ruthenium nitro complexes. On the other hand, kinetic rates are substantially altered, favorably in the case of ligand oxidation but adversely for eq 5. The results point both to a need to develop a better understanding of the effects of immobilization on chemical kinetics, and of how electrode immobilization can be exploited in such studies.

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(8) We have not attempted an analysis for the presumed phosphine oxide product owing to the extremely small amounts produced in these experiments.

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Heteropoly Periodates: Structure of $[Co_4{}^{3+}I_3{}^{7+}O_{24}H_{12}]^{3-}$ Ion and Principles Pertinent to a Separate Potentially Important Category of Heteropoly Complexes

Sir:

This paper (a) reports the structure of $[Co_4{}^{3+}I_3{}^{7+}O_{24}H_{12}]^{3-}$ ion, determined by X-ray crystallography, and (b) explains how this combines with other data to indicate existence of a sizable and potentially important new category of heteropoly complexes made up of $I^{7+}O_6$ octahedra sharing O atoms with numerous lower charged transition metal atoms. Such heteropoly periodate species should easily form derivatives having organic ligands and should undergo condensations and cocondensations into cross-linked or linear polymers via polyfunctional ligands.

Only about five elements [Mo, W, and V in their higher oxidation states plus, to more limited extents, Ta(V) and Nb(V)] have been reported as functioning significantly in heteropoly species as "addenda" atoms (i.e., the positive-valent element(s) present in high atomic proportions).[1] Thus, essentially all known heteropoly complexes contain several atoms of one or more of these few elements,[1-3] although about 50 other elements function as heteroatoms.

This paper proposes that there are three main characteristics which atoms must have to become heteropoly addenda: (a) small size relative to the radius ratio indicated for octahedral packing with oxygens, (b) ability to change readily in solution between tetrahedral and octahedral coordination with O, and (c) high positive charge. It is proposed that I(VII) atoms, having these characteristics, can function as interesting heteropoly addenda.

The size criterion was elucidated by the X-ray crystal structure of $K_5[Co^{3+}W_{12}O_{40}]\cdot 20H_2O$,[1,4,5] the first heteropoly structure wherein all of the anion's oxygens were directly located. W-O distances for the exterior unshared O's average 1.68 Å, while 2.38 Å is the average distance between a W and the interior O trans to the unshared one. Similar marked displacements of addenda atoms from the centers of their respective octahedra toward exterior O atoms of polyanions have been confirmed in our laboratory[6,7] and elsewhere[3,8] in numerous subsequent more accurate determinations.

The fact that addenda atoms are decidedly small relative to the octahedral pockets which enclose them, so that they can move off-center, is of paramount importance in explaining the very existence of discrete polyanions with definite structures, as well as in explaining their unusual properties. Interior O atoms in polyanions are more or less surrounded by positively charged atoms and consequently are not excessively polarized in any one direction. In contrast, exterior unshared O atoms have as nearest neighbors only distinctly positively charged addenda atoms, and so those oxygens become heavily polarized, inward, toward the addenda atoms. This creates very strong ion-induced dipole terms, and the small addenda atoms are therefore located very close to the exterior unshared O atoms, which are themselves drawn tightly inward. Being very heavily polarized toward the center of the complex, the exterior O atoms are (1) very poor at attaching protons (so heteropoly

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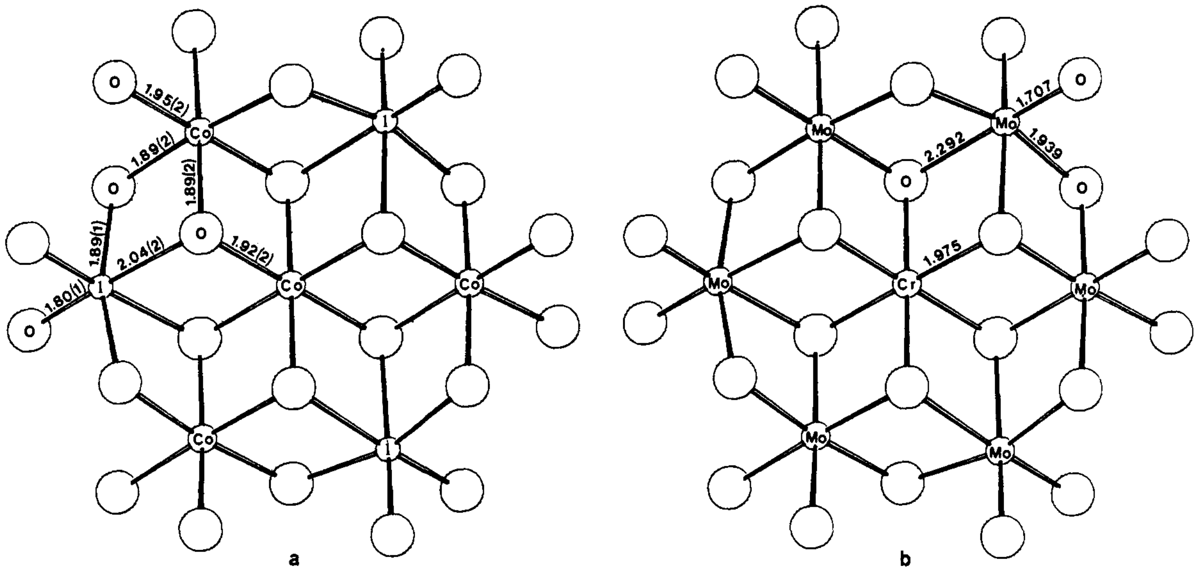

Figure 1. (a) $[Co_4{}^{3+}I_3{}^{7+}O_{24}H_{12}]^{3-}$ and (b) $[Cr^{3+}(OH)_6Mo_6{}^{6+}O_{18}]^{3-}$ (after Perloff[7]). Averages of bond lengths of each type are shown. H-bond patterns in a hydrated Na salt of b showed that the six H's are on the O's surrounding Cr. The CrO_6 is fairly compact owing to CFSE of d^3 Cr and the Cr–O distances are very regular. The Cr complexes, although weakly H bonded together via waters of crystallization, are directly attached to each other only via two weak Cr–O–H· ·O–Mo H bonds per complex, since the peripheral O's lack H atoms. In $[Li(H_2O)_4]_2H[Co_4I_3O_{24}H_{12}]{\cdot}3H_2O$ the much greater CFSE of d^6 Co enforces smaller CoO_6 octahedra and makes the Co–O distances nearly equal except for small elongation of the exterior Co–O bonds.[27] The 12 H's in the complex are on the six exterior O atoms of the outer Co's. The complexes are therefore directly held together into staggered sheets via 12 Co–O–H· ·O–I H bonds linking each anion to its neighbors. The H-bonding pattern slightly elongates the Co–O and I–O bonds to each peripheral O, in contrast to the Mo complex. The acid-salt H is found in an H_3O^+ ion. The large CFSE's of the Co's enforce a relatively rigid framework of four edge-sharing CoO_6 octahedra, which may contribute to shortening the interior I–O distances (relative to corresponding Mo–O distances) by holding the interior O's closer to the positions indicated for idealized octahedra. Also, the interior O–I distances are shortened because those O's are more susceptible to preferential polarization toward a single addendum (I^{7+}) than in the Mo complex (where two Mo's are nearest neighbors of each shared O). Nevertheless the addendum-type behavior of I^{7+} is clearly demonstrated. CFSE does not resist small angular distortions as much as variations in bond lengths. In this complex, as in all having this general structure,[3] the central octahedron is slightly flattened. In the past this has been attributed to coulombic repulsions between the addenda atoms. In view of the discussion in the text and the distances between addenda, we suggest that the ion-induced dipole *attractions* between addenda and outer O's are a much more significant cause of this flattening and of most other polyanion distortions which have in the past been attributed to repulsions between addenda.

acids are strong), (2) relatively poor at H-bond formation (so hydrodynamic radii are often essentially identical with crystallographic radii[9-11] and solvation energies are very low), (3) able to exert only weak van der Waals attractions (so lattice energies are low and solubilities in various solvents are explained). These considerations apply most strikingly to the larger and the nearly spherical (e.g., Keggin) structures or to ellipsoidal species like the 2:18 heteropolies, but they also apply well, with the logical modifications, to the smaller and the more disk-shaped species such as the Anderson-Evans[12] 6-heteropoly structures. Still more significant, the strong inward polarization of exterior O atoms acts, when these complexes form, to stop the polymerization reactions at the stages of discrete polyanion species. The distortions and polarizations also provide sizable stabilization energies for particular relatively limited structures. In contrast, most oxyanion monomers which polymerize upon acidification, in which the metal ions are too large to move off-center in their polyhedra, typically lead to infinite polymerizations and precipitates. Ta^{5+} and Nb^{5+} provide interesting borderline cases. They have radii which are small but decidedly larger than those of Mo^{6+}, W^{6+}, or V^{5+}. Nb^{5+} and Ta^{5+} consequently form fewer and less stable heteropoly complexes.

Change of coordination with O, the second necessary characteristic of an addendum atom proposed above, is indicated by mechanistic considerations. The mechanism of the first step of degradation of $[Cr^{3+}(OH)_6Mo_6O_{18}]^{3-}$ by OH^- was elucidated in our laboratory.[13,14] In important respects it is the inverse of the mechanism of the polymerization steps of $MoO_4{}^{2-}$ or $WO_4{}^{2-}$ by H^+, which has been described by Tytko and Glemser.[15] Each mechanism must require the addendum atom to change coordination between tetrahedral and octahedral.

It is well known that tetrahedral $IO_4{}^-$ and octahedral $IO_6{}^{-5}$ interconvert in aqueous solutions. The appropriateness of size of I^{7+} is shown by the present structure determination.

Other evidence is relevant to structural possibilities for heteropoly periodates. In 1966 our laboratory proved[16] that *one* addendum atom of a Keggin 12-heteropoly structure could be replaced by any of a variety of metals in lower oxidation state (e.g., Co^{2+}, Fe^{3+}, etc.), yielding the first heteropoly complexes containing two different heteroatoms.[17] This work was subsequently expanded upon.[18] In 1970 we proved[19] that the unshared O on the lower valent metal atom is really usually a water molecule, which can be replaced by another ligand (e.g., giving organic derivatives of heteropoly species[19] when organic ligands are used). Superficially, one might expect that the monosubstituted Keggin structures might easily react to replace a second of the structurally equivalent addenda [in one of the other 3-fold W_3O_{13} (or Mo_3O_{13}) groups] by a second lower valent metal atom. However, that is extremely difficult and may be impossible. The reasons may well include increase of overall negative charge as +6 valent atoms are replaced by ions in lower oxidation state(s). Structures containing $I^{7+}O_6$, however, should more easily tolerate additional octahedra containing lower charged transition metal ions adjacent to the IO_6's, because of the higher positive oxidation state of I^{7+}.

A Co(III) periodate complex, originally reported and differently formulated by Lister and Yoshino,[20] was reinvestigated, properly purified, and analyzed in 1961 by Nyman and Plane.[21] One of the present authors served as reviewer for the latter paper, and suggested that the evidence was consistent with a heteropoly structure of the Anderson-Evans[12] 6-heteropoly type, of formula $[Co_4I_3O_{24}H_{12}]^{3-}$. That suggestion was added in proof at the end of the paper.

In 1973 Ama, Hidaka, and Shimura[22] reacted ethylenediamine with the complex and obtained $[Co_4I_3O_{18}(en)_3]^{3-}$. This supported the proposed heteropoly-type structure and demonstrates, in view of the present X-ray structure, that the 12 H atoms in the parent complex are on water molecules coordinated at the unshared vertices of the three exterior CoO_6's. Those authors made similar complexes using other bidentate ligands, including L-alanine. The parent $[Co_4I_3O_{24}H_{12}]^{3-}$ anion and all of its derivatives with bidentate ligands should be optically active. Ama et al. obtained circular dichroism evidence for diastereoisomers in the L-alanine derivative.

We have repeated the Nyman and Plane potentiometric titrations of $H_3[Co_4I_3O_{24}H_{12}]$, showing three replaceable H's with virtually identical pK's (~1.5). We have shown by cryoscopy in fused $Na_2SO_4 \cdot 10H_2O$[13,23] that the complex is monomeric and very stable in solution. Its ligand field spectrum is typical of low-spin $Co^{III}O_6$.

Figure 1a shows[24] the X-ray structure for the anion in triclinic $[Li(H_2O)_4]_2H[Co_4{}^{3+}I_3{}^{7+}O_{24}H_{12}] \cdot 3H_2O$, space group $P\bar{1}$; $Z = 2$; $a = 10.163$ (2), $b = 16.572$ (4), $c = 9.624$ (1) Å; $\alpha = 105.61$ (2), $\beta = 114.77$ (3), $\gamma = 90.32$ (2)°; $R = 5.8\%$. Figure 1b shows Perloff's[7] structure for $[Cr^{3+}(OH)_6Mo_6{}^{6+}O_{18}]^{3-}$. Explanations are given in the figure caption.

Numerous new heteropoly structures should be possible wherein $I^{7+}O_6$ octahedra share O's with transition metal atoms, forming stable finite networks of various geometries. Since coordinated waters can be replaced by other ligands,[19,22] many organic derivatives should be possible. As with the present complex, ligands such as triethylenetetramine could be used to fasten the complexes together into interesting polymers.

We are investigating several heteropoly periodates. Some may be isomorphs of the Co complex described herein, but others have formulas indicating different structures. Details of the structure of the salt herein described will be published in a separate crystallographic paper.[27]

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(29) On leave from Regional Laboratory of Physical Chemical Analysis and Structural Research, Krakow, Poland; at Georgetown University, 1978–1980.

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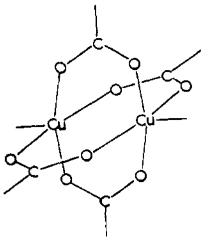
Bi- and Polynuclear Antiferromagnetic Metal Complexes (Cu, Ni) with Salicylaldimines and Acetate-Type Ligands. New Modes of Acetate Bridging

Sir:

Acetate bridging is well known[1] in compounds such as copper(II) acetate hydrate. The mode of bridging is shown in **1** and it links a pair of metal atoms, at relatively short distance. Salicylaldimine (sal)[2] and hydroxyl[3] ligands can also form bridges between metal atoms as shown in **2** and **3**. A question of immediate interest is how much versatility there is in the types of acetate bridging, and whether the different bridging ligands can all be mixed in the same complexes. For example, if binuclear complexes containing both acetates and other bridging ligands form readily, then this finding would support a controversial proposed mechanism whereby copper acetate, acting as a template, can distinguish between ribo- and deoxyribonucleosides.[4] The present results show that the answer to these questions is affirmative; acetate bridging is very versatile, and the different bridging ligands can indeed be mixed in the same complex. The complexes formed illustrate the three types of bridging mentioned above, as well as quite new ones. The first case, **4**, $pipH^+[Ni_2(PhenSal)_4(CH_3COO)]^-$, contains a normal acetate bridge of type **1** together with two salicylaldimine bridges, in addition to two nonbridging salicylaldimines. The acetate was introduced into normal $Ni(PhenSal)_2$ together with excess piperidine, which remains as the countercation. The structure was determined by X-ray crystallography ($R = 5.1\%$)[5], and Figure 1a shows the anion $[Ni_2(PhenSal)_4(CH_3COO)]^-$ and Figure 1b shows a schematic drawing of this ion. This is the first example of such a compound of nickel(II), although we have previously demonstrated by X-ray crystallography that salicylaldimines form stable binuclear nickel complexes that can be isolated in the solid state.[6] The formation reaction for complex **4** from $Ni(PhenSal)_2$ is given below:



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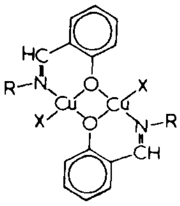

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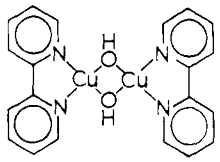

3

$$Ni(PhenSal)_2 \rightleftharpoons [Ni(PhenSal)_2]_2 \xrightarrow{CH_3COO^-} [Ni_2(PhenSal)_4(CH_3COO)]^- \quad (1)$$

The dimerization equilibrium in nickel salicylaldimines ($NiSal_2$) such as $Ni(PhenSal)_2$ has been demonstrated in

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