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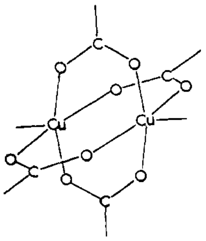
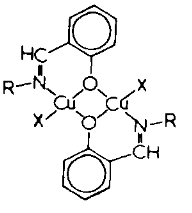
Bi- and Polynuclear Antiferromagnetic Metal Complexes (Cu, Ni) with Salicylaldimines and Acetate-Type Ligands. New Modes of Acetate Bridging

Sir:

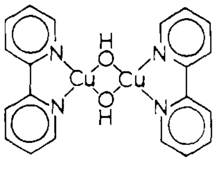
Acetate bridging is well known[1] in compounds such as copper(II) acetate hydrate. The mode of bridging is shown in **1** and it links a pair of metal atoms, at relatively short distance. Salicylaldimine (sal)[2] and hydroxyl[3] ligands can also form bridges between metal atoms as shown in **2** and **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:



1



2



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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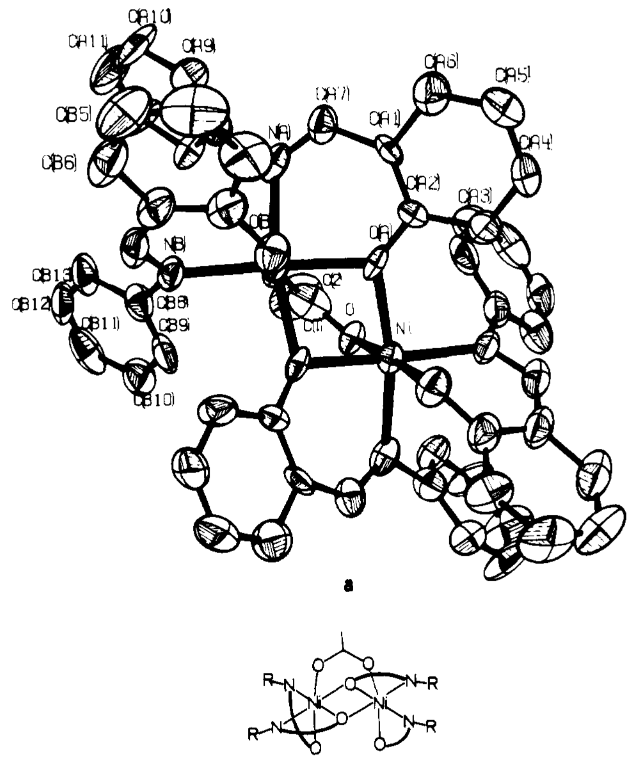

Figure 1. (a) Structure of $[Ni_2(PhenSal)_4CH_3COO]^-$ ion in complex **4**. Underside view of acetate bridge. (b) Schematic view of $[Ni(PhenSal)_4CH_3COO]^-$ ion. Side view of acetate bridge.

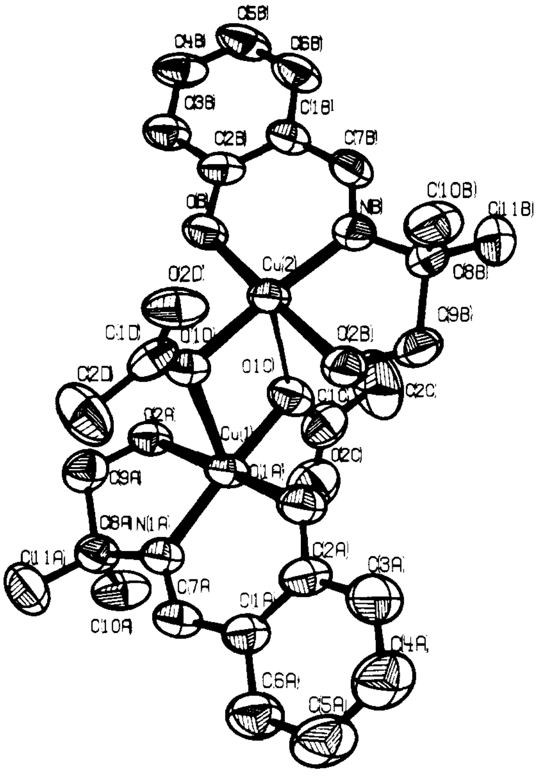

Figure 2. Molecular structure of complex **5**, $[Cu_2(i\text{-}PrOSal)_2(CH_3COO)_2]\cdot C_2H_5OH\cdot H_2O$.

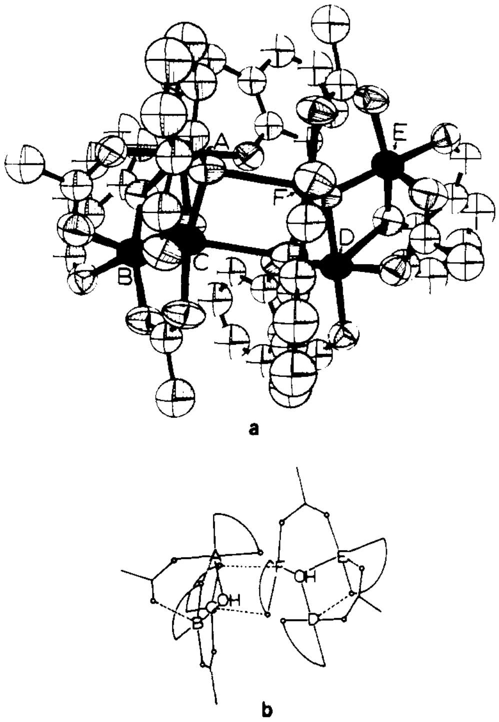

Figure 3. (a) Structure of complex **6**, $[Cu_3(OH)(EtSal)_3(F_3C\cdot COO)_2]_2^0$, with ethyl groups and fluorine atoms emitted and bonds to Cu atoms thickened. (b) Schematic diagram of complex **6** in the same orientation as in Figure 3a, showing the six copper atoms as A, B, C, D, E, and F.

variable temperature,[6] pressure,[7] and concentration[6] measurements, and the present reaction also demonstrates the existence of a significant proportion of dimeric species in solution. Complex **4** illustrates the kind of bridging and nonbridging salicylaldimine groups which must exist in the dimeric forms of $NiSal_2$ complexes. The complex anion **4** consists of two pseudooctahedral nickel species which share an edge, via the monoatomic Sal oxygen donors, plus a carboxylate bridge at an adjoining apex. The distance spanned is 3.101 (1) Å. The acetate ligand can be replaced by other bidentate anions and complexes of type **4** may be better templates for ribonucleosides than complex **1**,[4] for which it is not certain that the reaction would stop with the loss of one acetate rather than progressing on to complete dissociation.

The binuclear complex $[Cu_2(i\text{-}PrOHSal)_2(CH_3COO)_2]\cdot C_2H_5OH\cdot H_2O$ (**5**)[5] (Figure 2). (R = 5.2%) contains two unexpected single atom bridges, consisting in each case of one of the carboxylate oxygens between the two copper atoms. Although it is an obvious a priori possibility that copper dimers be bridged in this way, (analogous to the salicylaldimines, for example), the present structure is surprising. Normally the two oxygens of a carboxylate group each seek out a different metal atom in binuclear complexes, owing to the residual negative charge on each oxygen, to form Cu-O-C-O-Cu bridging as in **1**, instead of the Cu-O-Cu bridging of **5**. The distance spanned is 3.445 (1) Å. By bridging in this manner, the ligand is able to span larger distances than normally observed in the Cu-O-C-O-Cu bridges of **1**. However, type **1** bridges can span larger distances than is observed in the hydrated copper(II)[1] and anhydrous chromium(II)[9] acetates (2.616 and 2.288 Å, respectively). The nickel complex **4** in Figure 1 is an illustration of this fact. Complex **5** is bridged asymmetrically with the two acetate ligands having different copper-oxygen distances, owing to hydrogen bonding with the cocrystallized solvent molecules. The two copper atoms have different environments in the solid state, although in solution the compound is undoubtedly symmetrical. Complexes of type **5** are reaction intermediates of the formation reaction of dimeric[10] or tetrameric[11] complexes $[CuSal\cdot RO]_n$ (n = 2, 4) which have structural analogues:[12]

$$Cu_2(CH_3COO)_4 + SalH\text{-}R\text{-}OH \rightarrow \text{complex } \mathbf{5} \rightarrow [CuSal\cdot RO]_n$$

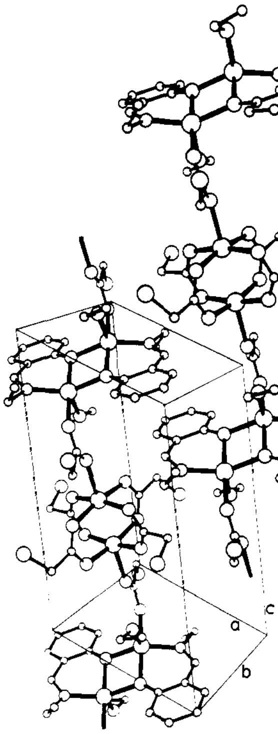

Figure 4. Unit cell of complex 7, [Cu$_2$(ClCH$_2$·COO)$_3$EtSal(C$_2$H$_5$OH)]$_\infty$, showing the packing of the polymeric chains in the lattice.

HSal·ROH represent the Schiff base condensates of salicylaldehyde derivatives with amino alcohols. When the reagents are mixed and heated, the final (brown) product is obtained after an initial immediate color change to green. Careful removal of the solvent without strong heating preserves the initial green color and deposits green crystals of type **5** complexes. These can be redissolved and heated to give the final product. This demonstrates that acetates and other bridging groups are readily interchanged, although the bridging is not necessarily in the conventional form as in **1**. Of the new complexes reported here, **5** is unique in exhibiting ferromagnetic exchange interactions. The others are all antiferromagnetic.

Complex **6**, [Cu$_3$(OH)(EtSal)$_3$(F$_3$C.COO)$_2$]$_2^0$ (R = 5.9%, refinement continuing),[5] is a hexanuclear copper(II) complex consisting of two independent oxygen-bridged Cu$_3$(OH) units with Cu atoms labeled A, B, C and D, E, F (Figure 3). The complex is a unique combination of hydroxyl, carboxylate, and salicylaldimine ligands. Each Cu$_3$(OH) fragment contains three independent and structurally different copper atoms. Despite the elaborate structure, the complex is quite stable, and can be dissolved and recrystallized in organic solvents without disproportionation into component ligands. The distances bridged in this case are 3.111 (1), 3.229 (1), and 3.398 (1) Å within the Cu$_3$(OH) unit A, B, C and 3.130 (1), 3.194 (1), and 3.471 (1) Å in D, E, F. The nearest metal-to-metal distances between the two Cu$_3$(OH) units is 3.359 (1) Å (C–F).

Complex **7**, [Cu$_2$(ClCH$_2$·COO)$_3$EtSal(C$_2$H$_5$OH)]$_\infty$ (R = 4.9%, refinement continuing) (Figure 4),[5] consists of two types of dimeric unit, [Cu$_2$(ClCH$_2$·COO)$_4$] with the standard structure **1** and Cu$_2$Sal$_2$X$_2$ with standard structure **2** (but containing a coordinated solvent molecule, C$_2$H$_5$OH), where X is ClCH$_2$·COO$^-$ and is attached via one of its carboxylate oxygen atoms. This leaves the other carboxylate oxygen, which is relatively electronegative, pointing away from the body of the Cu$_2$Sal$_2$X$_2$ dimeric unit to attach to the [Cu$_2$(ClCH$_2$·COO)$_4$] dimer. This linkage repeats to form an infinite chain -O-C-O-[Cu$_2$EtSal$_2$(C$_2$H$_5$OH)$_2$]-O-C-O-[Cu$_2$(ClCH$_2$·COO)$_4$]-O-C-O-. This mode of acetate bridging is also new, and unique to this kind of complex. The distances spanned are 2.629 (1), 3.062 (1), and 5.476 (1) Å within the [Cu$_2$(ClCH$_2$·COO)$_4$] dimer, within the [Cu$_2$EtSal$_2$(C$_2$H$_5$OH)$_2$] dimer, and between the two dimers, respectively.

The series of complexes **4**, **5**, **6**, and **7** demonstrates the versatility of salicylaldimine and acetate-type ligands in the chemically very closely related, yet structurally very different, complexes. The formate ion has been an apparent exception among carboxylates in its ready ability to form a variety of different bridges between metal atoms,[1,13] but evidently formate is not unique in this regard.

The single-crystal X-ray crystallographic work was carried out by countermethods as described previously.[14]

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Supplementary Material Available: Positional and thermal parameters for complexes **4**, **5**, **6**, and **7** (8 pages). Ordering information is given on any current masthead page.

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One-Electron Oxidation of Benzyltrialkylstannanes. 1. Cation Radical Fragmentation by Dual Modes

Sir:

Reactions of group 4a organometallics (R$_3$MR′, M = Si, Ge, Sn, Pb; R, R′ = alkyl) with tetracyanoethylene (TCNE; charge transfer, eq 1) or iridium(IV) complexes (one-electron transfer, eq 2) have been shown by Kochi and co-workers[1] to involve the intermediacy and fragmentation of cation radicals (eq 3). In all cases examined, the rate-determining step was

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