STRUCTURES AND PHYSICAL PROPERTIES OF POLYNUCLEAR CARBOXYLATES

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I. Introduction

Over 20 years have passed since the discovery (*1*) that the magnetic interaction of a pair of Cu^{2+} ions could produce an abnormal EPR spectrum for copper(II) acetate monohydrate, and the confirmation of this by an outline X-ray crystallographic determination (*2*) of the molecular structure to be the dimer $Cu_2(H_2O)_2(CH_3CO_2)_4$. Since then there have been many studies of the synthesis, properties, and bonding of copper(II) carboxylates and their complexes. This review summarizes these results and correlates the information provided by different techniques.

Besides the many dimers, the Cu^{2+} ion forms a number of other polynuclear structures containing carboxylate groups. These are also surveyed here as are studies on polynuclear carboxylates of other elements. Most of the work has been carried out on *d*-block transition elements but appropriate compounds of *f*-block or nontransition elements are also included. The review is restricted to clusters containing bridging carboxylate groups but is not confined to molecules in which carboxylates are the only bridging groups. Polymeric compounds are excluded unless their structures can be considered as an aggregate of clusters, since in other polymers the physical properties do not show marked cooperative effects. These restrictions involve some arbitrary exclusions, but we have violated our own selection rules when we have needed to draw comparisons between the properties of different types of structure, as in the section on vibrational spectra.

In addition to summarizing our knowledge of carboxylate clusters, the review describes the contributions made by different physical techniques, in the hope that the uses and limitations of these techniques will be revealed.

An earlier review (*3*) surveyed the complete range of simple carboxylates but excluded some more complex structures. Some earlier work on carboxylates is included in a survey (*4*) of magnetically abnormal copper(II) compounds. Carboxylates are discussed in a number of general reviews on "metal–metal bonds," but there have been many advances since the latest (*5*, *6*) of these.

II. Structures

This section is restricted to compounds whose structures have been unambiguously determined by crystallographic methods. Many other structures have been deduced from spectroscopic or magnetic results, often as a dubious speculation. These will be described in the section corresponding to the technique used.

Four types of carboxylate bridge have been identified, and these are shown in Fig. 1. Three of these involve both oxygen atoms of a carboxylate group, but only the syn-syn configuration brings the metal atoms close enough to form a clustered structure. The anti-anti and anti-syn configurations form polymeric structures. The monatomic bridge always accompanies other bridges and is never the only link between metal atoms. In some structures ligands other than carboxylate help to form the bridges between the metal atoms.

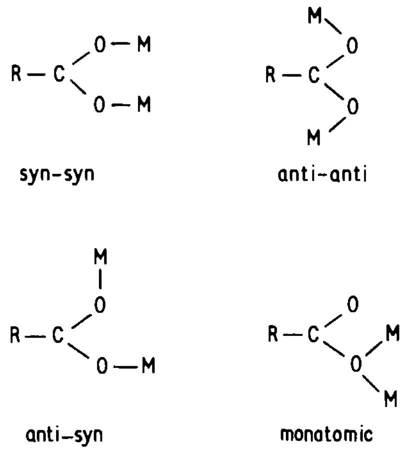


FIG. 1. The four types of carboxylate bridge.

A. BINUCLEAR COPPER(II) CARBOXYLATES

The earlier two-dimensional X-ray structural analysis (*2*) of copper(II) acetate monohydrate has been improved by three-dimensional studies with neutron diffraction (*7*) and X-ray diffraction (*8*). The structure (Fig. 2) consists of centrosymmetric dimer units with four bidentate acetates forming syn-syn bridges between the copper atoms and the water molecules coordinating along the Cu—Cu axis.

The most striking feature of the structure is the close approach of the 2 copper atoms (~2.615 Å) which is only a slightly longer separation than that in metallic copper (2.56 Å). Each copper atom is displaced

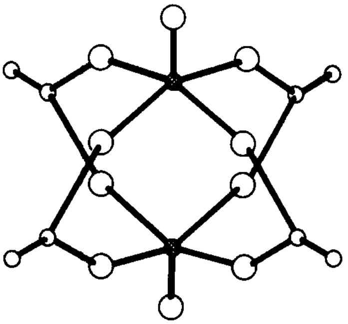


FIG. 2. Structure of $Cu_2(H_2O)_2(CH_3CO_2)_4$. Cross-hatched, Cu; large circles, O; small circles, C. [After Martin (*85*), by permission.]

TABLE I

Mean Structural Parameters for Binuclear Copper(II) Carboxylates, $Cu_2L_2(RCO_2)_4$

No.	R	L[a]	Cu—Cu (Å)	Cu—O (Å)	Cu—L (Å)	C—O (Å)	Cu—Cu—L (°)	O—C—O (°)	Cu—O—C (°)	Bridge length (Å)	Ref.
1	CH_3	H_2O	2.614	1.967	2.162	1.260	—	124.9	122.8	6.45	(*7*)
			2.616	1.969	2.156	1.260	—	124.8	123.1	6.46	(*8*)
2	CH_3	Py[b]	2.645	1.96	2.186	1.25	—	125.6	—	6.42	(*9*)
3	CH_3	Py[c]	2.630	1.98	2.126	1.24	—	125	124	6.44	(*10*)
4	CH_3	Quin	2.642	1.93	2.17	1.24	—	130	—	6.34	(*11*)
5	CH_3	NCS^-	2.643	2.03	2.08	1.24	—	126	123	6.54	(*12*)
6	CF_3	Quin	2.886	1.972	2.109	1.242	177.74	129.3	124.5	6.41	(*13*)
7	CH_2Cl	2-Pic	2.747	1.975	2.161	1.25	—	127	—	6.45	(*14*)
8	C_6F_5	THF	2.66	1.97	2.14	—	—	—	—	—	(*15*)
9	2-BrC_6H_4	H_2O	2.624	1.99	2.17	1.26	176.5	124	125	6.50	(*16*)
10	H	Urea	2.657	1.95	2.11	1.27	174.0	122	125	6.45	(*17*)
11	H	NCS^-	2.716	1.983	2.09	1.244	—	128.4	122.7	6.45	(*12*)
12	H	$\frac{1}{2}$ Dioxane	2.58	1.96	2.26	1.24	—	129	—	6.40	(*18*)
13	C_2H_5	—	2.578	1.95	2.28	1.28	—	—	—	6.46	(*19, 20*)
14	n-C_3H_7	—	2.565	1.982	2.245	1.232	—	120.1	—	6.46	(*19, 21*)
15	Succinate	H_2O	2.610	1.975	2.102	1.262	—	124.2	—	6.47	(*22*)
16	Acetylsalicylate	Acetyl residue	2.617	1.963	2.241	1.26	176	126	122.8	6.44	(*23*)

[a] Ligand abbreviations: Py = pyridine, Quin = quinoline, 2-Pic = 2-picoline, THF = tetrahydrofuran.

[b] Orthorhombic form.

[c] Monoclinic form.

from the plane of the 4 oxygen atoms by 0.22 Å toward the water molecules and away from the other copper atom. The 4 acetate groups are all planar, with normal bond distances and angles. There are eight intermolecular hydrogen bonds with each dimer unit interacting with four neighbors.

A list of structural parameters for $Cu_2(H_2O)_2(CH_3CO_2)_4$ and other binuclear copper(II) carboxylate complexes is given in Table I. Compounds numbered 1–11 have isolated dimeric molecules, but compounds 12–16 have binuclear units bridged together by other functional groups in the anion, by another donor atom in the axial ligand, or by monatomic oxygen bridges.

Two forms of $Cu_2(py)_2(CH_3CO_2)_4$ have been identified. The orthorhombic form (*9*) possesses a center of symmetry, but in the monoclinic form (*10*) the arrangement of dimeric units creates a twofold rotation axis through the copper atoms and pyridine molecules. The planes of the pyridine rings are inclined to each other at 60°, and there are slightly shorter Cu—Cu and Cu—N distances.

In anhydrous copper(II) propionate (*19*, *20*) and butyrate (*19*, *21*), the $Cu_2(RCO_2)_4$ dimers are linked by apical copper–oxygen interactions of about 2.28 Å to give a zig-zag chain of copper atoms (Fig. 3).

The binuclear units in copper(II) succinate dihydrate are covalently bonded by bridging succinate groups to form infinite chains with a network of hydrogen bonds connecting the chains (*22*).

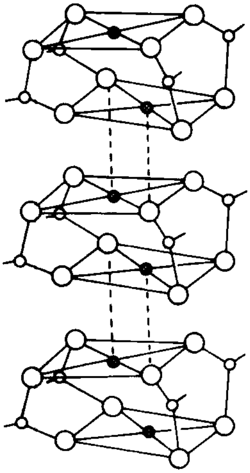


FIG. 3. Structure of polymeric $Cu(RCO_2)_2$. Cross-hatched, Cu; large circles, O; small circles, C. [Adapted with permission from *J. Amer. Chem. Soc.* **95**, 1164 (1973). Copyright by the American Chemical Society.]

In $[Cu_2(C_4H_8O_2)(HCO_2)_4]$ the 2 oxygen atoms of a dioxan molecule link neighboring dimeric units (*18*). In copper(II) acetylsalicylate, the oxygen atoms of the acetyl residue act as the terminal ligand, giving the polymeric structure (*23*). It is interesting to note that the copper–copper distances in the dimeric units of the polymeric structures are generally shorter than those of the discrete dimers.

B. OTHER BINUCLEAR CARBOXYLATES

Besides making the first determination (*2*) of the molecular structure of $Cu_2(H_2O)_2(CH_3CO_2)_4$, van Niekerk *et al.* (*24*) noticed a close resemblance between this structure and that of the chromium analog. The structure of the chromium compound was not refined below $R = 0.26$, and the dimensions were assumed identical to those of the copper dimer. A later redetermination (*25*) showed the Cr—Cr distance to be 2.362(1) Å, much shorter than earlier supposed and indicating strong metal–metal bonding. Table II lists structural parameters for this and other binuclear carboxylates for metals other than copper.

Compounds with 4 bridging carboxylate groups all have similar structures to $Cu_2(H_2O)_2(CH_3CO_2)_4$, including the cyclopentadienyl vanadium(III) complexes, in which the pentahaptocyclopentadienyl group can be considered to occupy one coordination site. For the uncomplexed molybdenum(II) carboxylates, the axial coordination site is occupied by an oxygen atom from a neighboring molecule. In $Mo_2(CF_3CO_2)_4$ this Mo—O distance of 2.72(1) Å was thought (*29*) too long to represent a bonding interaction. In $Ru_2Cl(C_3H_7CO_2)_4$ the chlorine atoms occupy the axial position for 2 ruthenium atoms, forming zig-zag chains. The Ru—Cl—Ru angle was not stated but from the authors' diagram (*33*) appears to be about 125°.

In binuclear compounds with fewer than 4 bridging carboxylate groups, the vacant coordination sites are occupied by monodentate halogen or carbonyl groups or polydentate dimethylglyoximate or norbornyl ligands. The structure of $Ag_2(CF_3CO_2)_2$ includes a nearly planar eight-membered ring of 2 silver atoms and 2 carboxylate groups (*44*). The cerium, erbium, and uranium complexes include nonbridging carboxylate groups as well as the 2 bridging carboxylate ions (*45–47*). In the erbium compound, 1 oxygen atom of each bridging group can be considered to coordinate both erbium atoms at distances of 2.39 and 2.60 Å (*46*) (Fig. 4). The $Sn_2(C_6H_5)_4(CH_3CO_2)_2$ molecule has five-coordinate tin atoms with the bridging carboxylate groups occupying the axial positions of a trigonal bipyramid and two Sn—C and one Sn—Sn bonds occupying the equatorial positions (*48*) (Fig. 5). The

TABLE II

STRUCTURAL PARAMETERS FOR CARBOXYLATE-BRIDGED DIMERS $M_2L_x(RCO_2)$ [M ≠ Cu]

Compound	M—M (Å)	M—O (Å)	M—L (Å)	C—O (Å)	M—M—L (°)	Ref.
Four carboxylate bridges						
$V_2(C_5H_5)_2(CF_3CO_2)_4$	3.704	2.05	2.28[a]	1.26	—	*(26)*
$V_2(C_5H_5)_2(C_4H_3OCO_2)_4$	3.625	2.04	2.29[a]	1.23	—	*(27)*
$Cr_2(H_2O)_2(CH_3CO_2)_4$	2.362	2.024	2.272	1.265	175.6	*(25)*
$Mo_2(CH_3CO_2)_4$	2.11	2.10	—	1.28	—	*(28)*
$Mo_2(CF_3CO_2)_4$	2.090	2.06	—	1.25	—	*(29)*
$Mo_2(py)_2(CF_3CO_2)_4$	2.129	2.116	2.548	1.26	171.0	*(30)*
$Re_2Cl_2(C_6H_5CO_2)_4 \cdot 2CHCl_3$	2.235	2.02	2.489	1.30	177.1	*(31)*
$[Re_2(ReO_4)_2(C_3H_7CO_2)_4]_n$	2.251	2.01	2.18	1.27	175.0	*(32)*
$Ru_2Cl(C_3H_7CO_2)_4$	2.281	2.00	2.587	1.28	175.1	*(33)*
$Co_2(quin)_2(C_6H_5CO_2)_4$	2.832	2.37	2.102	1.26	168.3	*(34)*
$Rh_2(H_2O)_2(CH_3CO_2)_4$	2.3855	2.039	2.310	1.269	176.47	*(25)*
Three carboxylate bridges						
$[Re_2Cl_2(i\text{-}C_3H_7CO_2)_3]^+ReO_4^-$	2.259	2.02	2.28	1.29	166.7	*(35)*
Two carboxylate bridges						
$[Re_2Cl_4(CH_3CO_2)_2] \cdot 2H_2O$	2.224	2.00	2.30	—	—	*(36)*
$Re_2I_4(C_6H_5CO_2)_4$	2.197	2.016	—	1.30	—	*(37)*
$Re_2(Ph_3P)_2(C_2H_5CO_2)_2OCl_3$	2.51	[b]	[b]	1.26	—	*(38)*
$Os_2(CO)_6(CH_3CO_2)_2$	2.731	2.076	1.82	1.29	170.5	*(39)*
$Rh_2(Rh_3P)_2(DMG)_2(CH_3CO_2)_2$[c]	2.618	2.088	2.485	—	173	*(40)*
$[Ni_2(nor)_2(CH_3CO_2)_2]$[d] (orthorhombic)	2.984	1.954	1.955[a]	1.256	—	*(41)*
$[Ni_2(nor)_2(CH_3CO_2)_2]$[d] (monoclinic)	3.079	1.932	1.971[a]	1.239	—	*(42)*
$[Pd_2(nor)_2(CH_3CO_2)_2]$[d]	2.960	2.152	2.043[a]	1.25	—	*(43)*
$Ag_2(CF_3CO_2)_2$	2.967	2.241	—	1.227	—	*(44)*
$(CN_3H_6)^+[Ce_2(H_2O)_2(CH_3CO_2)_8]^{2-}$	4.55	2.55	[e]	[f]	—	*(45)*
$Er_2(H_2O)_8(CH_3CO_2)_6$	—	2.39	—	—	—	*(46)*
$U_2O_4(Ph_3PO)_2(CH_3CO_2)_4$	—	2.36	[g]	1.32	—	*(47)*
$Sn_2(C_6H_5)_4(CH_3CO_2)_2$	2.69	2.25	2.25	1.26	—	*(48)*
One carboxylate bridge						
$Re_2(Ph_3P)_2(C_2H_5CO_2)OCl_5$	2.522	[h]	[h]	1.27	—	*(49)*

[a] Shortest M—C distance.

[b] Re—O(bridge), 1.92; Re—Cl(bridge), 2.40; Re—Cl(terminal), 2.36; Re—P, 2.46 Å.

[c] DMG = dimethylglyoximate.

[d] nor = 2-methylallyl-3-norbornyl.

[e] Ce—O(CH_3CO_2), 2.54; Ce—O(H_2O), 2.52 Å.

[f] Oxygens inequivalent: C—O, 1.22 and 1.30 Å.

[g] U—O(CH_3CO_2), 2.39; U—O(Ph_3PO), 2.37 Å.

[h] Re—O(bridge), 1.89; Re—Cl(bridge), 2.41; Re—Cl(terminal), 2.33; Re—P, 2.49 Å.

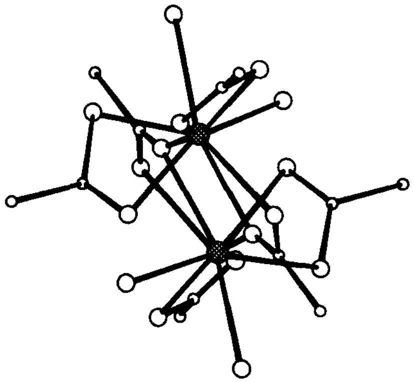


FIG. 4

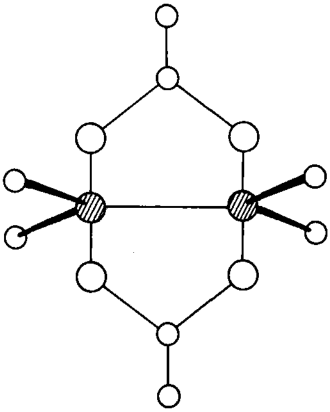


FIG. 5

FIG. 4. Structure of $M_2(H_2O)_8(RCO_2)_6$. Cross-hatched, M; large circles, O; small circles, C. [After Aslanov *et al.* (*46*).]

FIG. 5. Structure of $Sn_2R_4(RCO_2)_2$. Hatched, Sn; large circles, O; small circles, C.

compounds $Re_2(Ph_3P)_2(C_2H_5CO_2)_{(1 \text{ or } 2)}OCl_{(5 \text{ or } 3)}$ contain bridging oxygen and chlorine atoms as well as the carboxylate bridges (*38*, *49*).

There is much variation in the separations of the 2 metal atoms in the different compounds, from 2.090 Å in $Mo_2(CF_3CO_2)_4$ (*29*) to 3.704 Å in $V_2(C_5H_5)_2(CF_3CO_2)_4$ (*26*). Most of the short distances occur in compounds of the 4*d* and 5*d* transition elements. Cotton (*6*) has used molecular orbital theory to calculate bond orders ranging from 1 in rhodium(II) and osmium(I) to 4 in molybdenum(II) and rhenium(III). This approach also demonstrates the equivalence of the ruthenium atoms in $Ru_2Cl(C_3H_7CO_2)_4$ and of the rhenium atoms in $Re_2(Ph_3P)_2(C_2H_5CO_2)_2OCl_3$, so that in these compounds the metals show oxidation states of 2.5 and 3.5, respectively. The Sn—Sn distance of 2.69 Å in $Sn_2(C_6H_5)_4(CH_3CO_2)_2$ is considered (*48*) appropriate for an Sn—Sn single bond.

The interpretation of the metal–metal distances in dimeric carboxylates of 3*d* metals is not so simple. In most cases these cannot represent strong bonds as the molecules are paramagnetic, with the exception of the chromium(II) dimers. Nevertheless, there must be some interaction between the metal atoms as the magnetic susceptibilities are all lower than those found for mononuclear compounds of the same ion. This topic is discussed further in Section III.

It is interesting to note that the M—M—L angle is significantly different from 180° in dimeric carboxylates, although this dimension is not always reported. Generally, a shorter M—L distance gives a greater deviation from linearity. This may sometimes be attributed to nonbonding interactions. Thus in $Co_2(quin)_2(C_6H_5CO_2)_4$ the carbon atom next to the nitrogen in the heterocyclic ring is only 3.03 Å distant from one of the oxygen atoms. This oxygen atom is the one furthest from the cobalt atom, at 2.072 Å, whereas the other Co—O distances are close to their average of 2.025 Å *(34)*.

C. TRINUCLEAR CARBOXYLATES

Trinuclear carboxylates are commonest for trivalent metals, and most have structures derived from the triangular cluster $[M_3L_3O(RCO_2)_6]^+$ (Fig. 6). An oxygen atom is located at the center of an equilateral triangle of metal atoms. Two carboxylate groups bridge each pair of metal atoms, and a monodentate ligand is coordinated to each metal atom to give these an octahedral configuration. Table III lists the major structural parameters for triangular carboxylates.

In the compound commonly known as "anhydrous manganic acetate" the axial ligands are an acetic acid molecule and 2 acetate groups. The acetate groups are bonded to two more triangular clusters to give a polymeric structure *(52)*. In the compounds $M_3L_3O(CH_3CO_2)_6$

TABLE III

STRUCTURAL PARAMETERS FOR TRIANGULAR CARBOXYLATES

Compound	M—M (Å)	M—O[a] (Å)	M—O[b] (Å)	M—L[c] (Å)	O—C—O (°)	Ref.
$[Cr_3(H_2O)_3O(CH_3CO_2)_6]^+Cl^-\cdot 6H_2O$	3.28	1.97	1.89	2.02	125	*(50)*
$[Fe_3(H_2O)_3O(CH_3CO_2)_6]^+ClO_4^-$	3.29	2.02	1.91	2.08	120	*(51)*
$[Mn_3(CH_3CO_2H)(CH_3CO_2)_{2/2}O(CH_3CO_2)_6]_n$	3.3	[d]	[d]	[d]	116–132	*(52)*
$Mn_3(py)_3O(CH_3CO_2)_6$	3.35	2.04	1.94	2.05	—	*(53)*
$Fe_3(py)_3O(CH_3CO_2)_6$	3.29	2.04	1.91	2.19	—	*(54)*
$Ru_3(Ph_3P)_3O(CH_3CO_2)_6$	3.329	2.06	1.92	2.414	126	*(55)*
$Pd_3(CH_3CO_2)_6$	3.154	1.99	—	—	126	*(56)*
$Pd_3(CH_3CO_2)_3[(CH_3)_2CNO]_3\cdot 0.5C_6H_6$	3.009	2.03	[e]	—	129	*(57)*
$Co_3(dme)_3(CF_3CO_2)_3ClSO_4$ [f]	3.786	2.05	[f]	2.14	—	*(58)*

[a] M—O (acetate) distance.

[b] M—O (central) distance.

[c] Metal-axial ligand distance.

[d] Range for all Mn—O: 1.85–2.35 Å.

[e] Pd—O (acetoximate), 2.05 Å; Pd—N, 1.97 Å.

[f] dme = 1,2-dimethoxyethane; Co—Cl, 2.48 Å; Co—O (sulphate), 2.00 Å.

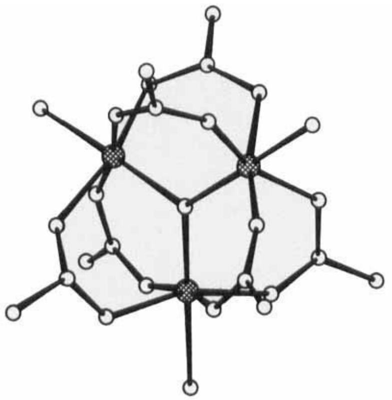


FIG. 6

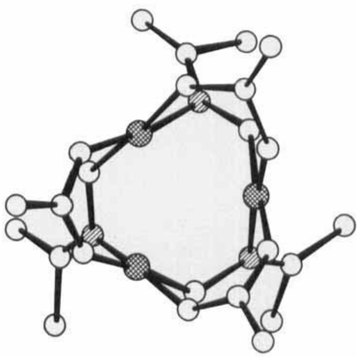


FIG. 7

FIG. 6. Structure of the $[M_3L_3O(RCO_2)_6]^+$ unit. Cross-hatched, M; open circles, nonmetals. [After Martin (*85*), by permission.]

FIG. 7. Structure of the $Pd_3(CH_3CO_2)_3[(CH_3)_2CNO]_3$ unit. Cross-hatched, Pd; hatched, N; open circles, O or C. [After Mawby and Pringle (*57*), *Chem. Comm.* p. 560 (1970), by permission.]

(L = py, M = Mn or Fe; L = Ph_3P, M = Ru), all 3 metal atoms are in similar environments, giving an oxidation state of 2.67 (*53–55*).

For divalent metals the structure of the triangular cluster is modified. In palladium(II) acetate, there are no axial ligands and the central oxygen atom is missing (*56*). The Pd—Pd separation is slightly shorter than the metal–metal separations in the oxygen-centered clusters, but it is too long to be considered a direct metal–metal bond. The structure of $Pd_3(CH_3CO_2)_3[(CH_3)_2CNO]_3{\cdot}0.5C_6H_6$ is derived from that of $Pd_3(CH_3CO_2)_6$ by replacing 3 acetate groups above one face of the Pd_3 triangle by acetoximate groups forming diatomic NO bridges (*57*) (Fig. 7). The benzene molecule is not coordinated.

The cobalt(II) complex $Co_3(dme)_3(CF_3CO_2)_3ClSO_4$ has a triangular structure in which all the anions act as bridging ligands (Fig. 8). The trifluoroacetate groups lie along the sides of the Co_3 triangle; the chlorine atom is equidistant from each cobalt atom and 1.15 Å away from the Co_3 plane; the sulfate ion is located on the opposite face of the Co_3 triangle from the chlorine atom, with 3 of its oxygens bonded to the cobalt atoms to give a tripodlike configuration. The dimethoxyethane ligands act as bidentate groups to give each cobalt atom six-coordination (*58*).

Only one complex carboxylate shows a linear array of 3 metal atoms. In the structure of $Co_3(quinoline)_2(C_6H_5CO_2)_6$(Fig. 9) (*59*), a quinoline

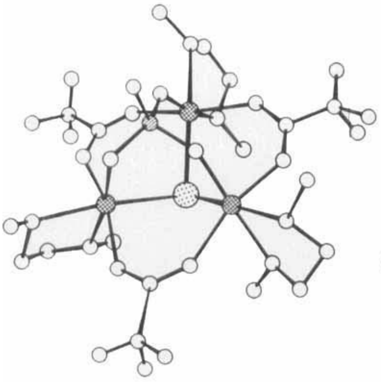


FIG. 8

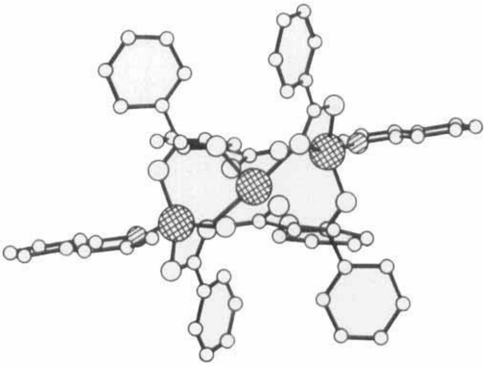


FIG. 9

FIG. 8. Structure of $Co_3(dme)_3(CF_3CO_2)_3ClSO_4$. Cross-hatched, Co; hatched, S; stippled, Cl; open circles, other nonmetals. [After Estienne and Weiss (*58*), by permission.]

FIG. 9. Structure of $Co_3(quinoline)_2(C_6H_5CO_2)_6$. Cross-hatched, Co; hatched, N; large circles, O; small circles, C. [From Catterick *et al.* (*59*), by permission.]

molecule and three benzoate ions form a distorted tetrahedron round each terminal Co^{2+} ion (Co—N, 2.108 Å; Co—O, 1.975 Å; N—Co—O, 92°–104°; O—Co—O, 111°–121°). The 2 terminal cobalt atoms are each linked to the central cobalt ion by three benzoate bridges, giving the central cobalt octahedral coordination (Co—O, 2.110 Å; O—Co—O, 90°). The cobalt–cobalt separation of 3.56 Å is greater than that in the dimer $Co_2(quin)_2(C_6H_5CO_2)_4$ formed by the same constituents. The nitrogen atoms are not exactly located on the Co—Co axis, the Co—Co—N angle being 164° (*34*).

D. TETRANUCLEAR CARBOXYLATES

Six different types of structure have been reported for carboxylates containing a cluster of 4 metal atoms. Of these, $Cu_4(CF_3CO_2)_4 \cdot 2C_6H_6$ alone has only carboxylate bridges (*60*). The structure (Fig. 10) is based on a Cu_4 rhombus with sides of ca. 2.8 Å and angles of 113.1° and 66.8°. A trifluoroacetate group bridges each adjacent pair of Cu^+ ions, with opposite pairs of anions lying on the same side of the Cu_4 plane to give nearly linear coordination of the copper atoms (O—Cu—O = 162°–175°). The shortest copper–benzene contact is 2.7 Å, which the authors believe represents a π-bond from a C=C bond to give three-coordination.

Compounds $M_4O(RCO_2)_6[M = Be$ (*61*), Zn (*62*), $R = CH_3$; M = Co (*63*), $R = (CH_3)_3C]$ have a tetrahedral cluster of metal atoms with the

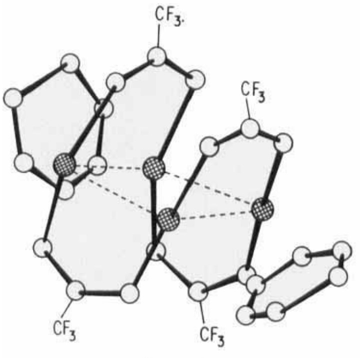


FIG. 10

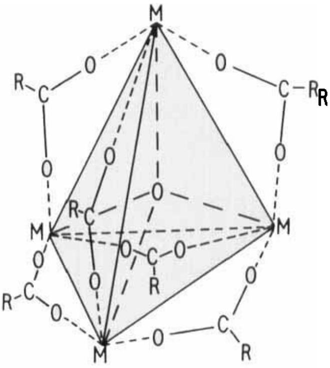


FIG. 11

FIG. 10. Structure of $Cu_4(CF_3CO_2)_4{\cdot}2C_6H_6$. Cross-hatched, Cu; open circles, O or C. [After Rodesiler and Amma (*60*), by permission.]

FIG. 11. Structure of $M_4O(RCO_2)_6$.

oxygen atom at the center of the tetrahedron and a carboxylate bridge along each edge, giving approximately tetrahedral coordination for the metals (Fig. 11).

Another molecule containing a tetrahedron of cobalt atoms is $Co_4(CH_3CO_2)_2(CH_3O)_4(C_5H_7O_2)_4$ (Fig. 12) (*64*). The cobalt atoms and triply bridging methoxide groups occupy alternate corners of a cube. The acetate groups are located outside two opposite faces of the cube,

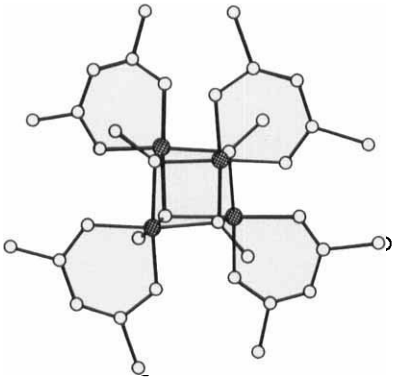


FIG. 12. Part of the structure of $Co_4(CH_3CO_2)_2(CH_3O)_4(C_5H_7O_2)_4$. Cross-hatched, Co; open circles, O or C. The acetate groups are removed to show the Co_4O_4 cube more clearly. [After Bertrand and Hightower (*64*). Adapted with permission from *Inorg. Chem.* **12**, 206 (1973). Copyright by the American Chemical Society.]

and each cobalt atom is chelated by an acetylacetonate ion to give octahedral coordination. For 2 of the cobalt atoms, the Co—O distances are not greater than 1.94 Å, but, for the other 2, the Co—O distance is not less than 1.99 Å. The former must show oxidation state III and the latter oxidation state II, but it is curious that the 2 similar cobalt atoms are not at opposite corners of the Co_4O_4 cube, but instead are the pairs joined by acetate bridges. The inequivalence is also shown by the angles of the Co_4O_4 cube.

The structure of $Cu_4(quinoline)_4(OH)_2(CF_3CO_2)_6$ is shown schematically in Fig. 13. There are two types of copper atom, both in square-pyramidal coordination. In one pair, the copper atoms are bonded to 2 hydroxyl ions, 2 bridging carboxylates, and a quinoline molecule. The environment of the other 2 copper atoms consists of the other oxygens on the bridging carboxylates, 1 hydroxyl ion, 1 monodentate carboxylate, and a quinoline molecule. In this arrangement the hydroxyl ions act as triply bridging ligands and the closest approach of the copper atoms is 2.996 Å (*65*).

The tetranuclear complex $Co_4R_2(OH)_2(CH_3CO_2)_2(H_2O)_2(C_2H_5OH)_2$, where R is the binucleating ligand 4-hydroxy-bis-3,5-[*N*-(2′-hydroxyphenyl)formimidoyl], contains 2 cobalt(II) and 2 cobalt(III) atoms, with hydroxyl and acetate bridges as well as that provided by the binucleating ligand (*66*).

Compound $Pt_4(NO)_2(CH_3CO_2)_6 \cdot 2CH_3CO_2H$ contains a rectangular Pt_4 unit (Fig. 14) with sides of 2.944 and 3.311 Å. The shorter sides have two carboxylate bridges; the longer sides have one carboxylate bridge

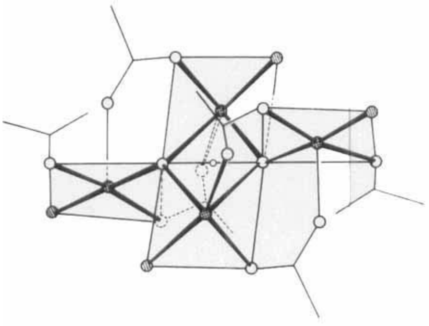


FIG. 13

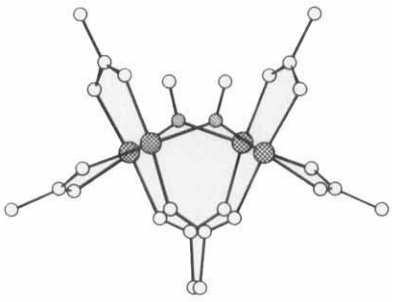


FIG. 14

FIG. 13. Structure of $Cu_4(quinoline)_4(OH)_2(CF_3CO_2)_6$. Cross-hatched, Cu; hatched, N; open circles, O. [After Little *et al.* (*65*). Adapted with permission from *J. Amer. Chem. Soc.* **96**, 3834 (1974). Copyright by the American Chemical Society.]

FIG. 14. Structure of $Pt_4(NO)_2(CH_3CO_2)_6$. Cross-hatched, Pt; hatched, N; open circles, O or C. [After de Meester and Skapski (*67*), by permission.]

and one NO bridge. The angles of 120° at the nitrogen atom indicate that this ligand is negatively charged to give the platinum atoms an oxidation state of II. The acetic acid molecules are hydrogen bonded in pairs but are not coordinated (*67*).

E. POLYMERIC CARBOXYLATES

Some polymeric compounds have structures closely related to known dimers or trimers and have been discussed earlier. This section deals with other polymeric compounds, and these are listed in Table IV.

TABLE IV

STRUCTURES OF POLYMERIC CARBOXYLATES

Compound	Bridge types	M—M (Å)	Ref.
$Cu(HCO_2)_2$ (royal blue)	Anti-syn	3.44	(*68*)
$Cu(H_2O)_2(HCO_2)_2$	Anti-syn	—	(*69*)
	Anti-anti	—	
$[(CH_3)_2NH_2]^+[Cu(HCO_3)_3]^-$	Anti-anti	—	(*70*)
$Cu(H_2O)_2(HCO_2)_2{\cdot}2H_2O$	Syn-syn	—	(*71*)
$Cu(4\text{-}CH_3C_6H_4NH_2)(C_2H_5CO_2)_2$	Syn-syn	3.197	(*72*)
	Monatomic		
$Cu(H_2O)_3(C_6H_5CO_2)_2$	Syn-syn	3.15	(*73*)
$CuCH_3CO_2$	Syn-syn	2.556[a]	(*74, 75*)
	Monatomic		
$Ce(H_2O)_{0.7}(CH_3CO_2)_3$	Syn-syn	—	(*76*)
	Monatomic		
$U(CH_3CO_2)_4$	Syn-syn	—	(*77*)
	Monatomic		
$Mn(H_2O)_4(CH_3CO_2)_2$	Syn-syn	3.6	(*78*)
	Anti-anti	—	
	Anti-syn	—	
	Monatomic		

[a] Value from Mounts *et al.* (*74*); 2.544 Å in Drew *et al.* (*75*).

To achieve substantial cooperative effects in physical properties, metal ions must be brought close together by bridging in the syn-syn configuration (Fig. 1). In the polymeric carboxylates with bridging in the anti-syn or anti-anti configurations, there are only slight cooperative effects and long metal–metal separations. Only structures with syn-syn bridging will be described in detail.

The copper atoms in copper formate tetrahydrate are coordinated by 4 oxygen atoms from different formate groups (Cu—O, ca. 2.0 Å) to give a polymeric sheet. The water molecules are sandwiched between the sheets but only half of them are coordinated (Cu—O, 2.36 Å), the others being linked to the structure by hydrogen bonds (*71*).

The interpretation of the magnetic properties (Section III) of monoaniline complexes of copper(II) carboxylates was confused by the erroneous assumption that they had the dimeric structure. In fact their structure is a linear chain polymer (Fig. 15), found originally in the copper(II) propionate-4-toluidine complex. Each copper atom has a square-pyramidal configuration, coordinated by 4 propionate groups and 1 aniline molecule. Two of the propionates form syn-syn bridges to a neighboring copper atom, and the other two form monatomic

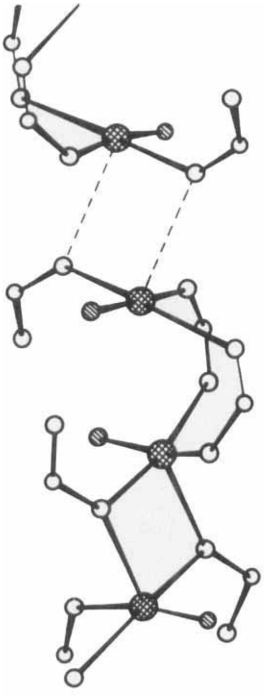


FIG. 15

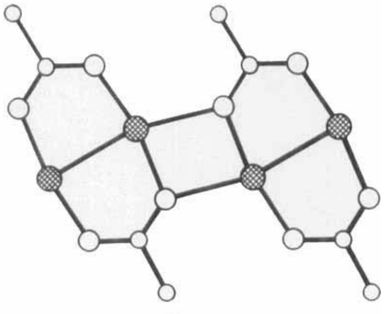


FIG. 16

FIG. 15. Structure of Cu(4-toluidine)$(C_2H_5CO_2)_2$. Cross-hatched, Cu; hatched, N; open circles, O or C. [After Yawney *et al.* (*72*). Adapted with permission from *J. Amer. Chem. Soc.* **95**, 1164 (1973). Copyright by the American Chemical Society.]

FIG. 16. Structure of $CuCH_3CO_2$. Cross-hatched, Cu; large circles, O; small circles, C. [After Mounts *et al.* (*74*). Adapted with permission from *Inorg. Chem.* **13**, 802 (1974). Copyright by the American Chemical Society.]

bridges to another copper atom. The copper–copper separations are much longer than those found in dimeric copper(II) carboxylates, in keeping with greater Cu—O—C angles (average 130°) (*72*).

In $Cu(H_2O)_3(C_6H_5CO_2)_2$ only half the benzoate ions are bonded to the copper atoms, which are coordinated by 4 water molecules and 2 bridging benzoate groups to give a linear chain (*73*).

The structure of copper(I) acetate (Fig. 16) contains a polymeric unit based on a planar, eight-membered ring of 2 copper atoms and 2 carboxyl groups (Cu—O, 1.92 Å). One oxygen from each acetate group also forms a monatomic bridge to another copper atom (Cu—O, 2.31 Å). The copper–copper separation of 2.556 Å is suitable for a direct bond between the copper atoms to give an unusual, planar four-coordination for Cu(I) (*74*, *75*).

The combination of syn-syn and monatomic bridging is also found in the two structures of polymeric carboxylates of *f*-block elements. In $Ce(H_2O)_{0.7}(CH_3CO_2)_3$ the cerium atoms are nine-coordinate with 2 acetate groups acting as bidentate ligands and 2 acetate ions acting as both syn-syn and monatomic bridges with neighboring cerium atoms (*76*).

The structure of uranium(IV) acetate has four syn-syn bridges between neighboring uranium atoms in a linear chain (U—O, 2.52 Å) (Fig. 17), but the O_8 prism is distorted so as to introduce two other

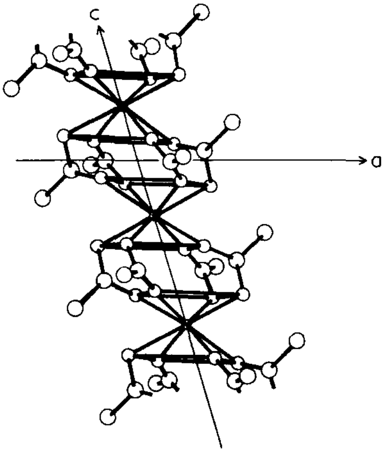


FIG. 17

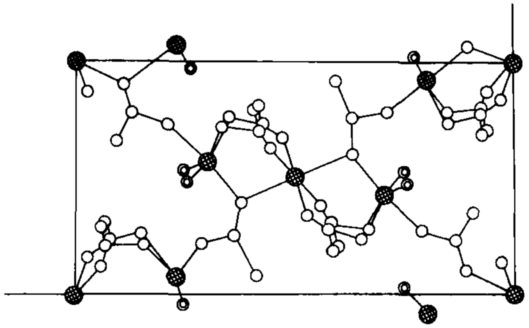


FIG. 18

FIG. 17. Structure of $U(CH_3CO_2)_4$. The U atoms lie along the *c* axis. [From Grdenić and co-workers (*77*), by permission.]

FIG. 18. Structure of $Mn(H_2O)_4(CH_3CO_2)_2$. Cross-hatched, Mn; double circles, H_2O; open circles O or C. [After Bertaut *et al.* (*78*), by permission.]

significant U—O contacts of 2.80 Å and give the uranium atoms ten-coordination (*77*).

Finally, $Mn(H_2O)_4(CH_3CO_2)_2$ is unique in exhibiting all four modes of bridging (Fig. 18) (*78*). It is interesting that this compound has a structure that differs from those of the mononuclear cobalt and nickel analogs (*79*).

III. Magnetic Susceptibility Measurements

A. Copper(II) Carboxylates

As long ago as 1915, Lifschitz and Rosenbohm (*80*) measured the magnetic moment of copper(II) acetate monohydrate at room temperature as 1.4 μ_B, which was lower than the spin-only value of 1.73 μ_B as well as being lower than the values of 1.8 to 2.2 μ_B usually found for copper(II) compounds. The first study (*81*) of the temperature dependence of the single-crystal susceptibilities showed that there was a maximum in the susceptibility near 270 K, contrary to the expectations of the Curie law. A later study (*82*) of the powdered hydrate between 87 and 288 K also indicated the existence of a maximum in the susceptibility, but there were quantitative disagreements between the two sets of data. This disparity was probably due to impurities of mononuclear compounds, a common source of error in this field. Later Figgis and Martin (*83*), using measurements up to 400 K, found maxima at 255 K for the hydrate and 270 K for the anhydrous compound, but the magnetic moment decreased continuously with the temperature (Fig. 19).

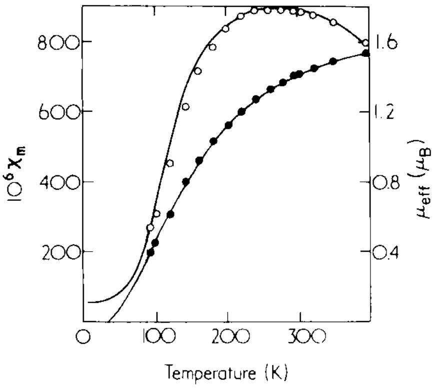


Fig. 19. Temperature dependence of the magnetic susceptibility (open circles) and moment (closed circles) of $Cu_2(H_2O)_2(CH_3CO_2)_4$. [After Martin (*85*), by permission.]

Meanwhile, Bleaney and Bowers (*1*), having investigated the monohydrate's anomalous EPR spectrum (Section IV), suggested that the anomalous susceptibility arose from the coupling of isolated pairs of copper atoms by exchange forces. The electron spins interact to form two energy levels. These are a singlet state, in which the spins are antiparallel, and, at slightly higher energy, a triplet state with the spins parallel. The characteristic shape of the susceptibility–temperature curve reflects the thermal distribution of the molecules over these energy states. At the lowest temperatures the singlet state is more abundant, but as the temperature rises the triplet state becomes increasingly populated, giving a rise in susceptibility up to its maximum, after which the Curie law is followed and the susceptibility falls at higher temperatures.

The mathematical treatment of this process has often been reviewed (*84–89*) and need only be outlined here. The spin Hamiltonian describing the exchange is

$$\mathscr{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2 \tag{1}$$

where J is the exchange integral, and $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spins of the separate metal ions. The eigenvalues obtained, recognizing the vectorial nature of the spins, are

$$E(S') = -J[S'(S'+1) - 2S(S+1)] \tag{2}$$

where

$$S' = (S_1 + S_2), (S_1 + S_2 - 1), \ldots, (S_1 - S_2) \quad \text{and} \quad S = |S_1| = |S_2|.$$

For the copper(II) dimers, S' takes values of 1 or 0, giving an energy separation of the two states of $-2J$, assuming J to be negative with the singlet state lower in energy. Some workers have used $-J$ as the singlet–triplet separation, but happily this practice now appears to be obsolete.

The magnetic moment is given by summing the squares of the individual moments for all spin states, which are weighted by the appropriate Boltzmann factor:

$$\mu^2 = g^2 \frac{\sum_{S'} S'(S'+1)(2S'+1)\omega(S')\exp[-E(S')/kT]}{(2S'+1)\omega(S')\exp[-E(S')/kT]}\,{\mu_B}^2 \tag{3}$$

where g, k, and T have their usual meanings, and $\omega(S')$ is the number of states having the given value of S': $\omega(S')$ is unity for both states of the copper(II) dimer.

For the copper(II) dimer, Eq. (3) reduces to

$$\mu^2 = g^2\left[\frac{3\exp(2J/kT)}{1 + 3\exp(2J/kT)}\right]\mu_B{}^2 \tag{4}$$

and the molar susceptibility per copper atom is given by

$$\chi_M = \frac{g^2N\beta^2}{3kT}\left[\frac{1}{1 + \frac{1}{3}\exp(-2J/kT)}\right] + N_\alpha \tag{5}$$

where N_α is the second-order paramagnetism, 60×10^{-6}.

By differentiating Eq. (4) with respect to temperature, Figgis and Martin (*83*) established the relationship:

$$2J = -1.6\,kT_N \tag{6}$$

where T_N is the temperature of maximum susceptibility, the Néel temperature.

Thus, we obtain $2J$ values of $-286\ \mathrm{cm}^{-1}$ for $Cu_2(H_2O)_2(CH_3CO_2)_4$ and $-302\ \mathrm{cm}^{-1}$ for $Cu_2(CH_3CO_2)_4$, in good agreement with the values caculated from Eq. (5) using N_α equal to 60×10^{-6} and g values of 2.13 and 2.17, respectively. However, the factor of -1.6 should be replaced (*85*) by -1.247, reducing the values of $2J$ to -221 and $-235\ \mathrm{cm}^{-1}$. The best procedure is to use Eq. (5) with g values determined from EPR spectra and N_α calculated from the electronic absorption spectrum, with J as the only variable. Any inconsistencies can be attributed to impurities of magnetically dilute compounds, which are usually very hard to eliminate. Some workers have used values of g and J that vary with temperature, but a study (*90*) of the temperature dependence of the three principal susceptibilities of a single crystal of the monohydrate showed that these could be interpreted with a single value of J, $g_\perp$, and $g_\parallel$.

Since the early investigations of $Cu_2(H_2O)_2(CH_3CO_2)_4$, there have been very many magnetic studies of other compounds of the type $Cu_2L_2(RCO_2)_4$. These have been thoroughly listed recently (*91*) and will not be repeated here; we shall discuss only compounds having some special features of interest. The magnetic properties of presumably dimeric copper(II) carboxylates, which have been reported since the compilation of Jotham *et al.* (*91*), are collected in Table V, but only studies including temperature variations are included.

The possession of a low and temperature-dependent magnetic moment has been used as the principal criterion for assigning a dimeric

TABLE V

MAGNETIC PROPERTIES OF DIMERIC COPPER(II) CARBOXYLATES

Compound[a]	T (K)	μ_B	T (K)	μ_B	g	$-2J$ (cm^{-1})	Ref.
$Cu_2(ICH_2CO_2)_4$	303	1.44	93	0.44	2.18	280	(*92*)
$Cu_2D(ICH_2CO_2)_4$	303	1.44	93	0.43	2.18	280	(*92*)
$Cu_2(CH_3CHFCO_2)_4$	303	1.66	93	1.0	2.20	167	(*93*)
$Cu_2D(CH_3CHFCO_2)_4$	293	1.30	93	0.54	2.21	384	(*93*)
$Cu_2(CH_3CCl_2CO_2)_4$	303	1.50	93	0.64	2.17	252	(*94*)
$Cu_2D(CH_3CCl_2CO_2)_4$	303	1.44	93	0.46	2.16	267	(*94*)
$Cu_2D(CH_3CH_2CO_2)_4$	293	1.34	93	0.34	2.17	333	(*95*)
$Cu_2(H_2O)_2(ClCH_2CH_2CO_2)_4$	303	1.45	93	0.48	2.22	322	(*95*)
$Cu_2D(ClCH_2CH_2CO_2)_4$	293	1.35	93	0.35	2.18	346	(*95*)
$Cu_2(CH_3CHClCO_2)_4$	293	1.44	93	0.47	2.13	302	(*95*)
$Cu_2D(CH_3CHClCO_2)_4$	293	1.43	93	0.40	2.20	326	(*95*)
$Cu_2(H_2O)_2(BrCH_2CH_2CO_2)_4$	293	1.42	93	0.39	2.22	340	(*95*)
$Cu_2D(BrCH_2CH_2CO_2)_4$	293	1.40	93	0.39	2.19	325	(*95*)
$Cu_2(CH_3OH)_2(BrCH_2CH_2CO_2)_4$	293	1.42	93	0.47	2.18	318	(*95*)
$Cu_2(CH_3CHBrCO_2)_4$	293	1.45	93	0.45	2.18	293	(*95*)
$Cu_2D(CH_3CHBrCO_2)_4$	293	1.44	93	0.40	2.22	304	(*95*)
$Cu_2(BrCH_2CHBrCO_2)_4$	293	1.48	93	0.47	2.22	283	(*95*)
$Cu_2D(BrCH_2CHBrCO_2)_4$	293	1.47	93	0.47	2.18	292	(*95*)
$Cu_2A_2(CH_3CO_2)_4$	293.1	1.44	79.5	0.20	—	—	(*96*)
$Cu_2A_2(C_6H_5CO_2)_4$	293.6	1.40	79.5	0.235	—	—	(*96*)
$Cu_2A_2(HO{\cdot}C_6H_4{\cdot}CO_2)_4$	294.4	1.44	80.0	0.25	—	—	(*96*)
Cu_2A_2(*o*-cresotinate)$_4$	293.6	1.43	80.0	0.19	—	—	(*96*)
Cu_2A_2(*m*-cresotinate)$_4$	293.4	1.39	80.5	0.19	—	—	(*96*)
$Cu_2(THF)_2(C_6F_5CO_2)_4$	298	1.49	98	0.16	—	—	(*97*)

[a] D = dioxane; A = antipyrine.

structure to a copper(II) carboxylate. An example is the study (*98*) of the copper(II) salts of the unsaturated acids, acrylic, vinylacetic, and allylacetic, with room temperature moments of 1.38, 1.35, and 1.43 μ_B, respectively.

Early measurements (*99*, *100*) of the room temperature magnetic moments of copper(II) α,ω-dicarboxylates, $Cu[O_2C(CH_2)_nCO_2]$, showed they were not magnetically dilute. The temperature dependence (*101*) of the susceptibility of the oxalate ($n = 0$) showed a very broad maximum at 260 K, but the values were all in the range 546 × 10^{-6} to 626 × 10^{-6} between 98 and 356 K. This behavior is like that observed (*102*) in $CuCl_2$ and $CuBr_2$, in which chains of halide-bridged copper atoms are linked by other halogen bridges. Therefore, possible structures of bridged dimeric units were proposed. The malonate ($n = 1$)

deviated only slightly from the Curie law and consequently was formulated as monomeric, although an anti-anti bridging polymeric structure is also possible. The variation of susceptibility with temperature for copper(II) succinate ($n = 2$), glutarate ($n = 3$), and adipate ($n = 4$) was similar to that of copper(II) acetate, suggesting that the intervening methylene groups insulate neighboring dimeric units. This proposal was confirmed by the determination (22) of the crystal structure of copper(II) succinate dihydrate (Section II,A).

The hydrates of $Cu(HCO_2)_2$ show varied behavior (*103*) between 80 and 360 K. The dihydrate and royal blue anhydrous forms are magnetically dilute, but the tetrahydrate and the blue and the turquoise anhydrous forms have slightly subnormal magnetic moments of 1.64, 1.61, and 1.76 μ_B, respectively, at room temperature. This difference in behavior between the formates and other carboxylates matches the different structures adopted by the formates, which have layers of copper atoms in bridged polymers (*68*, *69*, *71*).

The occurrence of different structures for copper(II) alkanoates can be correlated (*104*, *105*) with the pK_a's of the acids; the anions of weaker acids form dimers more readily. It was suggested that, because of the proximity of the copper atoms in the dimer, this structure will be less stable if a large residual positive charge remains on the copper atoms after bonding with the carboxylate groups. If the available σ-electron density on the oxygen atoms of the anion is low, the large residual charge on the copper atoms favors the anti-anti or anti-syn configurations. For example, the pK_a^{298} of formic acid is 3.75 but that of acetic acid is 4.76. In addition to electrostatic repulsion, the higher effective charge on the copper atoms will contract the *d* orbitals and potentially reduce the orbital overlap in the dimeric unit.

Studies of arylcarboxylates offer more scope for exploring the effects of varying the pK_a of the acid group. However, the results are often complicated by the apparent existence of different magnetic forms of one compound depending on the preparative method. Thus, there are a total of eleven values reported (*106*–*109*) for the room temperature magnetic moment of copper(II) benzoate, the figures ranging from 1.39 to 1.87 μ_B. In this case an EPR study (*110*) has shown that at least some of the variations are caused by the presence of mononuclear impurities in a dimeric compound. Nevertheless, it is reasonable to suppose that some copper(II) carboxylates may exist in genuinely isomeric forms. At the extremes of the pK_a range for arylcarboxylates, $Cu(4\text{-}CH_3C_6H_4CO_2)_2$ (pK_a, 4.35) has a room temperature magnetic moment of 1.4 μ_B, falling to 0.69 μ_B at low temperature (*108*, *111*), and $Cu(2,5\text{-}Cl_2C_6H_3CO_2)_2$ (pK_a 2.47) has a moment of 1.72 μ_B at 289.0 K, falling to 1.12 μ_B at 85.0 K (*112*).

Lewis *et al.* (*111*) concluded that substitution ortho to the carboxyl group favored formation of dimers in addition to the electronic factor. However, the operation of such steric effects cannot be simple since a study (*113*) of copper(II) nitrobenzoates showed that the 3-nitrobenzoate is a dimer and the 4-nitrobenzoate, a polymer despite these compounds having similar pK_a's of 3.47 and 3.41, respectively.

Another complication occurs in alkanoates in which the alkyl chain contains a donor group. The magnetic moment of $Cu(NCCH_2CO_2)_2 \cdot 0.5H_2O$ is 1.49 μ_B at 300 K and 1.04 μ_B at 173 K, indicating a dimeric structure (*114*), perhaps with the cyanide group occupying an axial position on a neighboring dimer. Yet, the hydrated copper(II) salts of methoxy-, ethoxy-, and phenoxyacetic acids are all magnetically dilute (*114*) and have been shown by X-ray structure determinations (*115, 116*) to be monomeric compounds with five-membered chelate rings.

Magnetic susceptibility measurements have shown that variations in the axial ligand may have a marked effect on the properties of copper(II) carboxylates. If the uncomplexed $Cu(RCO_2)_2$ already shows strong antiferromagnetism, the addition of a donor ligand to form $Cu_2L_2(RCO)_4$ results in only minor changes in the magnetic properties, even with strongly coordinating anions such as NCS^- or NO_2^- (*117*). On the other hand, copper(II) 1-naphthoate or 2-chlorobenzoate, which are only weakly antiferromagnetic and probably polymeric, form complexes with water or pyridine that have magnetic properties characteristic of a dimer (*109*).

The magnetic properties of the copper(II) acetate adducts with the sterically hindered amines, quinuclidine and triethylenediamine, raise an interesting and unresolved structural problem (*118*). At room temperature the magnetic moments are 2.06 and 1.94 μ_B, respectively, typical of magnetically dilute copper(II) compounds, but these fall to 0.0 and 0.41 μ_B at low temperature, which indicates strong antiferromagnetism.

For some years the magnetic properties of aniline or toluidine adducts of copper(II) carboxylates were anomalous in showing room temperature moments of 1.61 to 1.79 μ_B that fell to 1.24–1.50 μ_B at liquid nitrogen temperatures (*72, 101, 119, 120*), thus forming an intermediate group between the dimers and polymers. The X-ray determination (*72*) of the structure of $Cu(4\text{-}CH_3C_6H_4NH_2)(C_2H_5CO_2)_2$ showed the complex to be a polymer with some syn-syn bridging, which is associated with strong antiferromagnetism.

There have been a number of attempts to correlate the magnitude of J with recognizable features in the constituents of the dimeric carboxylates, but none of these efforts has proved very successful. Hatfield *et al.* (*121*) prepared a series of 1-butanol adducts of $Cu(4\text{-}RC_6H_4CO_2)_2$

with varying R groups designed to change the electronic effect but not the steric hindrance, but there was no consistent trend of J with pK_a or any substituent constants. Adducts of the type $Cu_2(C_2H_5OH)_2(4\text{-}RC_6H_4CO_2)_4$ all have room temperature magnetic moments of about 1.5 μ_B for R = Cl, Br, I, but for R = CN, F, or OH the same reaction conditions gave magnetically dilute compounds with the formula $Cu(OH)(RC_6H_4CO_2)$ (*122*).

Melnik (*123*) has observed that J values for halogen-substituted copper(II) propionates and their binuclear adducts with dioxane decrease in the order $BrCH_2CH_2CO_2 > CH_3CHBrCO_2 > BrCH_2CHBrCO_2$ and $ClCH_2CH_2CO_2 > CH_3CHClCO_2 > CH_3CCl_2CO_2$ and considered the σ-attracting effects of the halogen atoms to give weaker metal–oxygen covalent bonds and, therefore, decreased overlap of the orbitals containing the unpaired electrons. However, it will be seen later that simple overlap of metal orbitals is not a sufficient description of the exchange process.

Doedens (*124*) has tabulated the magnetic and structural results for the small minority of dimeric carboxylates for which both sets of results are available. It was not possible to find any correlation between magnetic moments of J values with metal–metal separation and only an approximate correlation with the length of the Cu—O—C—O—Cu bridge.

The best correlation available at present is that due to Kettle and co-workers (*91*) who noted that J was larger for alkylcarboxylates than for arylcarboxylates and that for axial ligands J values followed the trend: pyridine and its derivatives > alcohols, ethers, or acid derivatives > water > uncomplexed carboxylates.

At the moment these trends cannot be explained by a generally agreed theory of magnetic interactions. Figgis and Martin (*83*) suggested that a δ bond existed from overlap of the $3d_{x^2-y^2}$ orbitals of the copper atoms (Fig. 20), but this bond was much weaker than most

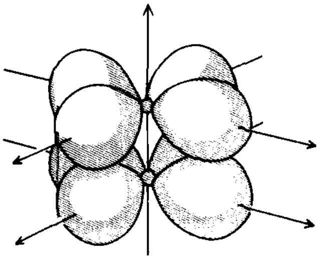


FIG. 20. The δ overlap in dimeric copper(II) carboxylates. [After Martin (*85*), by permission.

two-center covalent bonds. On the other hand, Forster and Ballhausen (*125*) favored a σ bond between the copper atoms using the d_{z^2} orbitals. Neither approach can be a complete description of the interaction between the copper atoms since there is also a large reduction in the magnetic moment for $V_2(C_5H_5)_2(RCO_2)_4$, where the vanadium atoms are separated by over 3.6 Å (*26, 27*).

A later model devised by Jotham and Kettle (*126, 127*) included both metal–metal bonding and spin exchange. They argued that when 2 electrons are allocated to two orbitals σ_1 and σ_2, six wave functions result:

$$\sigma_1\sigma_2 \quad \bar{\sigma}_1\bar{\sigma}_2 \quad \sigma_1\bar{\sigma}_2 \quad \bar{\sigma}_1\sigma_2 \quad \sigma_1\bar{\sigma}_1 \quad \sigma_2\bar{\sigma}_2$$

where $\sigma_1\bar{\sigma}_1$ represents 2 electrons in orbital 1 with opposite spins. They believed that the last two of the six had not been included in Bleaney and Bowers' (*1*) spin exchange treatment. Jotham and Kettle included a covalency term in the spin Hamiltonian, and their calculations involved two parameters, J and γ. The former is the spin–spin coupling constant, and γ is the covalency splitting parameter. The difference between their results and those obtained by Bleaney and Bowers (*1*) is shown in Fig. 21.

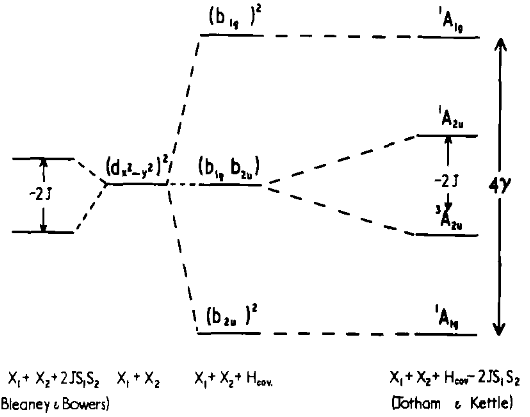


FIG. 21. Bonding schemes in dimeric copper(II) carboxylates.

Both methods give a spin–singlet ground state and a spin–triplet as the next excited state but differ in the origin of these levels. In Jotham and Kettle's model the ground state originates from the functions not previously considered and the spin exchange process is ferromagnetic even though the overall energy level pattern leads to antiferromagnetic behavior. The energy separation between the $^1A_{1g}$ ground state and the $^3A_{2u}$ excited state is now $(2\gamma - J)$, and the magnetic moment is given by

$$\underset{\text{(dimer)}}{\mu} = [(6g^2/F) + N_\alpha T]^{1/2}\,\mu_B \tag{7}$$

where $F = 3 + \exp(-2J/kT) + 2\exp(-2J/kT)\cdot\cosh(2\gamma/kT)$.

By substituting a value of g taken from the EPR spectrum and a calculated value of N_α, Jotham and Kettle believed that they obtained a very precise fit with the experimental susceptibility data for $Cu_2(H_2O)_2(CH_3CO_2)_4$ (*126*) and some of its homologs (*128*). The agreement was, indeed, better than that achieved by Figgis and Martin (*83*) at low temperatures, but it was worse above 300 K. A better fit at high temperatures was given by modifying the model to give energy states basically the same as those in the Bleaney–Bowers model but with an additional spin–singlet state that becomes appreciably thermally populated at higher temperatures (*129*). This singlet–triplet–singlet model was also applied to a wide range of copper(II) carboxylates (*91*), with some of the data condemned as unreliable since they did not fit the new theory.

However, it is not surprising that the new approach gave better results than the Bleaney–Bowers model, since it contains an additional adjustable parameter, which ought always to give better agreement with experimental data. The new values of J do not give a better correlation with the nature of the ligands than do the earlier set. In fact, the differences in susceptibility between the Jotham–Kettle and Bleaney–Bowers models are probably not great enough to be measured reliably by experiment. Of the sets of data studied, 43% gave a singlet–singlet separation of infinity, meaning that the Bleaney–Bowers model gave the best fit.

The validity of the Jotham–Kettle model was also doubted in an investigation (*12*) of the compounds $(Me_4N)_2[Cu_2(NCS)_2(RCO_2)_4]$, where $R = H$ or CH_3. Using Bleaney and Bowers's formula to fit the temperature variation of the magnetic susceptibility, the singlet–triplet separations were found to be 305 and 485 cm^{-1} for the acetate and formate, respectively. X-Ray crystallography showed that the copper–copper distance in the acetate is 2.643 Å and in the formate, 2.716 Å, so that the shorter distance corresponds to the weaker exchange, the opposite result to that expected from the metal–metal bonding approach.

An alternative model to direct bonding uses the concept of "superexchange" first proposed in another context by Anderson (*130*, *131*). As a π orbital of a bridging carboxylate group overlaps with both copper atoms the unpaired spins may migrate to the ligands and there become paired. Dubicki and Martin (*132*) showed that the π pathway could only be made available by mixing a $^2B_1$ state (hole in the $d_{x^2-y^2}$ orbital) on copper with a $^2B_2$ state (hole in the d_{xy} orbital), and this requirement would make the superexchange contribution small. Nevertheless, such a process has been used to explain the weak antiferromagnetism of polymeric copper(II) formate tetrahydrate (*103*) and must be a preferable explanation for the reduced magnetic moment of $V_2(C_5H_5)_2(RCO_2)_4$, where the vanadium–vanadium separations are over 3.6 Å (*26*, *27*). Superexchange was also advanced (*12*) as an explanation for the difference in magnetic data between the formate and acetate complexes $(Me_4N)_2[Cu_2(NCS)_2(RCO_2)_4]$, in which the greater value of $2J$ corresponds to the shorter path length through the bridging ligands. However, this comparison has been questioned (*90*) since the shorter Cu—O distance in the formate would give a smaller positive charge on copper and greater expansion and overlap of the *d* orbitals in a metal–metal direct interaction. An additional disadvantage to the superexchange concept is the qualitative nature of the discussions.

A molecular-orbital treatment may be able to reconcile the various disagreements by including overlap between metal orbitals and appropriate combinations of ligand orbitals in a quantitative calculation of energy levels. First results (*133*) show a satisfactory prediction of a singlet ground state and an accessible triplet excited state, but it is bound to be difficult to perform sufficiently sensitive calculations to rationalize the small variations in magnetic behavior between different dimeric copper(II) carboxylates.

It has been suggested (*134*) that the strong inductive effect of the Ph_3E groups (E = Si or Ge) in $Cu(H_2O)(Ph_3ECO_2)_2$ is responsible for reducing their magnetic moments to about 0.8 μ_B at 296 K, but it has not been shown crystallographically that these compounds really do have dimeric structures.

Magnetic data have been used to calculate equilibrium constants and thermodynamic data for the singlet–triplet equilibrium (*94*, *111*, *118*, *135*), assuming the singlet state to have a magnetic moment of zero and the triplet state a moment of 2.9 μ_B. Values of ΔH^0 obtained by this method agree with values of $-2J$ deduced from curve-fitting procedures.

Martin (*136*) suggested that the differing vibrational frequencies of the ground and excited spin states should introduce a modification in the Bleaney–Bowers treatment. This would give a reduction in $-2J$ for $Cu_2(H_2O)_2(CH_3CO_2)_4$ from 310 to 294 cm^{-1} if the Cu—Cu vibration had an energy of 100 cm^{-1} in the singlet state and 63 cm^{-1} in the triplet state. This modification has never been extended to other molecules.

Applying pressures of up to 3000 atm to saturated solutions of copper(II) carboxylates in chloroform or dichloromethane gave very little change in magnetic properties, indicating that there was very little change in volume between the singlet and triplet states. However, a solution of copper(II) decanoate in chloroform containing a 5 *M* proportion of pyridine had a magnetic moment of 1.46 μ_B at 9.67 atm and 1.57 μ_B at 1108 atm, indicating the existence of an equilibrium such as

$$Cu_2(RCO_2)_4 + \text{solvent} \rightleftharpoons 2Cu^{2+}\ (\text{solvated}) + 4RCO_2^-$$

with increased pressure favoring the more solvated species. An aqueous solution of copper(II) acetate has a moment of about 1.75 μ_B at all pressures, indicating complete dissociation (*137*).

The remaining polynuclear copper(II) carboxylate, whose magnetic properties have been investigated is $Cu_4(\text{quinoline})_4(OH)_2(CF_3CO_2)_6$, has a magnetic moment that falls from 1.60 to 1.05 μ_B over the temperature range 300–82.5 K. Its structure (Fig. 13) contains two different types of copper atom. The total spin of the system will range from 2 (fully parallel) to 0 (fully antiparallel), but, instead of the separations between the various energy levels being a function of a single coupling constant J, this problem requires coupling constants J_{12}, $J_{11'}$, and $J_{22'}$, where the pairs of similar copper atoms are labelled (1,1′) and (2,2′). To derive suitable values for the J parameters, g was taken to be 2.17 and $J_{22'}$ was assumed to be zero in view of the long separation of Cu_2 and $Cu_{2'}$; this procedure gives $J_{11'}$ to be $-90\ cm^{-1}$ and J_{12} to be $-70\ cm^{-1}$ (*65*). These are reasonable values since $Cu_{1'}$ is closer Cu_1 than is Cu_2 and since Cu_1 and $Cu_{1'}$ are linked by two monatomic bridges, whereas Cu_1 and Cu_2 are linked by one monatomic and two triatomic bridges. The authors also show that, although the molecule can be considered to be dimerized $Cu_2(\text{quin})_2(OH)(CH_3CO_2)_3$, the Bleaney–Bowers treatment for an isolated dimer does not fit the data (*65*).

B. OTHER BINUCLEAR CARBOXYLATES

The simple spin Hamiltonian given by Eq. (1) requires modification when more than 2 metal atoms interact or when their spins are greater than $\frac{1}{2}$. The general expression becomes

$$\mathscr{H} = -2 \sum_{ij} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \qquad (8)$$

where J_{ij} is the coupling constant between the spin, $\mathbf{S}_i$, on the ith atom and the spin, $\mathbf{S}_j$, on the jth atom. The rest of the calculation follows the

Bleaney–Bowers model (*1*), but the potential complexity of the problem is reduced if the metal atoms are in similar environments. This treatment is known as the Heisenberg–Dirac–van Vleck (HDVV) method after its originators (*138–140*), the Bleaney–Bowers method being a special case for 2 metal ions of spin $\frac{1}{2}$. The HDVV method is often successful in explaining the magnetic properties of polynuclear carboxylates but has limitations as a survey of the results will show.

The chromium(II) carboxylates were the first antiferromagnetic carboxylates to be studied, and an early report (*141*) recognized the diamagnetism of $Cr_2(H_2O)_2(CH_3CO_2)_4$. Since then many more chromium(II) carboxylates and complexes with formula $CrL(RCO_2)_2$ have been found to show magnetic moments less than 1 μ_B (*142–145*). As with the copper(II) dimers, the antiferromagnetism has been discussed from the superexchange and metal–metal bonding viewpoints. The short Cr—Cr separation of 2.363 Å indicates that direct metal–metal overlap may be more significant in these dimers. Chromium(II) formate appears to exist in a number of different forms, ranging in color from different shades of blue to red, the color of $Cr_2(H_2O)_2(CH_3CO_2)_4$. The room temperature magnetic moments of the blue forms are all over 4.4 μ_B, but the red form has a moment of 0.71 μ_B and is probably dimeric (*142*, *144*). The ease of oxidation to chromium(III) makes it very hard to obtain reliable magnetic data for these compounds.

The room temperature magnetic moments of vanadium(III) acetate and benzoate, which were found (*146*) to be $V_2(RCO_2)_6$ dimers in solution, are 0.77 μ_B, a much lower value than the spin-only value of 2.83 μ_B for magnetically dilute vanadium(III) compounds. However, the temperature and field dependence of the acetate's magnetism proved too complicated for detailed interpretation.

Following earlier work by King (*147*), there has been an extensive study (*26*, *148*, *149*) of the series $(C_5H_5)_2V_2(RCO_2)_4$ of which two examples have been shown crystallographically to be dimers. The acetate is typical (*26*) in having a room temperature magnetic moment of 1.71 μ_B falling to 0.56 μ_B at 83 K. The data fit an HDVV model with $J = 110\ cm^{-1}$. Because $(C_5H_5)Ti(C_6H_5CO_2)_2$ has magnetic moments of 0.95 and 0.53 μ_B at 295 and 80 K, it was believed to be dimeric, as was also $(C_5H_5)_2V(C_6H_5CO_2)_2$ with moments of 1.62 and 0.38 μ_B at 297 and 79 K, but for this molecule the disposition of the 2 additional cyclopentadienyl groups was not specified (*148*).

Although $Co_2(quin)_2(C_2H_5CO_2)_4$ has a dimeric structure (*34*), the interpretation of its magnetic properties is not simple. An HDVV treatment would give spin levels of 3, 2, 1, and 0 separated by multiples of J, but this calculation does not reproduce the fall in moment from 4.11 μ_B at 293 K to 1.71 μ_B at 98 K with a maximum in the susceptibility at 268 K. The difference can be attributed to the extensive spin–orbit coupling that is always shown by high-spin square-pyramidal cobalt(II) compounds and for which the HDVV treatment makes no allowances. Lines (*150*) studied this problem by considering the spin–orbit coupling on isolated Co^{2+} ions and then considering exchange coupling between the various spin states. This produces an extremely unwieldy calculation, but it can be simplified by calculating the exchange between only the ground doublets, the higher levels being included in a molecular field approximation that has the effect of making g temperature dependent. Ginsberg (*88*) has reviewed various approximations of Lines's approach, but none of these give a good fit to the data (*151*). Single-crystal susceptibilities are usually needed to interpret the magnetic properties of cobalt(II) compounds (*152*), and these data will be combined with a new angular overlap model for exchange (*153*).

Complex $Co(quin)(2\text{-}NO_2C_6H_4CO_2)_2$ exists in two forms. The green form is probably dimeric, having a magnetic moment of 4.12 μ_B at 298 K and 2.40 μ_B at 98 K with a maximum susceptibility near 173 K. There is also a less antiferromagnetic slate-blue form that, with moments of 4.23 μ_B at 298 K and 3.57 μ_B at 98 K, may be polymeric (*154*).

The dimeric carboxylates of the second- and third-row transition elements are very strongly coupled and are interpreted as showing direct, and often multiple, metal–metal bonding. Compounds having an even number of d electrons are diamagnetic. Examples are the molybdenum(II) carboxylates (*155*), adducts of rhodium(II) carboxylates (*156*, *157*), and the rhenium(III) compounds $ReCl(RCO_2)_2$ (*158*). The diamagnetism of many of these compounds has been used as a criterion of a dimeric structure in the absence of a crystal structure. The polymeric ruthenium(II, III) compound $[Ru_2(CH_3CO_2)_4]^+Cl^-$ (*159*) and other $Ru_2(RCO_2)_4X$ species ($R = CH_3, CH_2Cl, C_6H_5$; $X = Cl, Br, I, NCS, NO_3, CH_3CO_2$) (*160*) have magnetic moments of about 2.9 μ_B at room temperature that fall to 2.3–2.7 μ_B at 90–100 K. These values indicate the presence of 3 unpaired electrons on each pair of ruthenium atoms, but it is curious that the moments are higher than those usually observed for either ruthenium(II) or ruthenium(III) compounds.

C. TRINUCLEAR CARBOXYLATES

The first work on the trinuclear cations $[M_3OL_3(RCO_2)_6]^+$ was performed by Welo (*161*), who found they obeyed the Curie–Weiss law in the range 203–298 K with large antiferromagnetic Weiss constants of up to 695°. Kambe used (*162*) an HDVV model for an isosceles triangle of three spins, which allows 1 of the metal atoms to be in a different environment from the other 2. The resulting spin Hamiltonian is

$$\mathscr{H} = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_2 \cdot \mathbf{S}_3) - 2J'(\mathbf{S}_3 \cdot \mathbf{S}_1) \tag{9}$$

When $J' = 0$ the model represents a linear group of 3 metal atoms, and when $J' = J$ it represents an equilateral triangle. Welo's data were reasonably interpreted by assuming $2J = 2J' = -26$ and $-56\ \mathrm{cm}^{-1}$ for chromium(III) and iron(III), respectively, and the work led Orgel (*163*) to propose the structure of the cation which has been confirmed crystallographically (Section II,C).

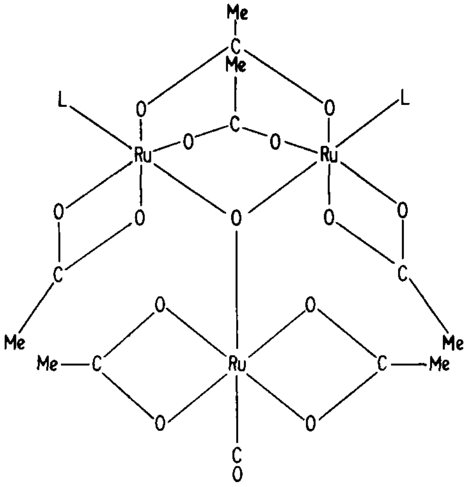
In later magnetic studies (*164–169*) of trinuclear carboxylates of chromium(III), manganese(III), and iron(III), some of the complexes were found to follow Eq. (9) well, but others often required J and J' to be different by up to 60%, although crystallographic studies have not shown such marked inequalities in the structures so far determined. It is possible that some of the alleged inequivalencies could be due to very small quantities of paramagnetic impurities, as many of the compounds are precipitated from aqueous solutions without recrystallization. The most studied chromium(III) complex of this series is $[Cr_3(H_2O)_3O(CH_3CO_2)_6]^+Cl^- \cdot 6H_2O$. In the cation, the Cr—O (water) distances of 1.95, 1.86, and 1.86 Å are the only hint of inequality (*50*), but the magnetic data (*165*) fit for an equivalent J of $-10.4\ \mathrm{cm}^{-1}$. A later study (*170*) of this salt suggests that the HDVV model is inadequate, but the fluorescence spectra (Section V,C) and heat capacity measurements (Section X) show that the compound contains equal numbers of two kinds of inequivalent cluster and that there is a phase transition at 211.4 K.

Although no crystallographic studies of trinuclear vanadium(III) carboxylates have been made, it is probable that the cation formulated (*171*) as $[V_3(ClCH_2CO_2)_6(OH)_2]^+$ really is $[V_3(H_2O)O(ClCH_2CO_2)_6]^+$ and that the compound formulated (*172*) as $V_3(OH)(CH_3CO_2)_8$ is really the vanadium analog of "anhydrous manganic acetate," i.e., $[V_3(CH_3CO_2H)(CH_3CO_2)_{2/2}O(CH_3CO_2)_6]_\infty$, as its magnetic properties approximately fit the HDVV treatment for an equilateral triangle of $S = 1$ ion, with $J = -15\ \mathrm{cm}^{-1}$ (*173*).

The structural unit $M_3L_3O(RCO_2)_6$ also occurs in a number of uncharged species in which the metal has the average oxidation state of 2.67 (M = Mn, Fe, Co). For $Mn_3(py)_3O(CH_3CO_2)_6$ the magnetic moment falls from 4.82 μ_B at 298 K to 3.76 μ_B at 123 K (*53*). Complexes $[Fe_3L_3O(CH_3CO_2)_6] \cdot nL$ ($L = H_2O$, $n = 2$; L = py, $n = 0.5$) are both antiferromagnetic (*174*). $Co(CH_3CO_2H)_3O(CH_3CO_2)_6$ is also antiferromagnetic, but its magnetic properties vary with the means of preparation, probably because of contamination with cobalt(II) species (*175*).

The trinuclear complex $Co_3(dme)_3(CF_3CO_2)_3ClSO_4$ follows a Curie–Weiss law between 160 and 360 K with a room temperature moment of 4.68 μ_B. As the compound contains octahedrally coordinated Co^{2+} ions, it resembles $Co_2(quin)_2(C_6H_5CO_2)_4$ in needing consideration of an orbital contribution to the magnetic properties (*58*).

A ruthenium(III) trimer with the formula $[Ru_3(H_2O)_3O(CH_3CO_2)_6]^+$-$(CH_3CO_2)^-$ is reported (*176*) to have a magnetic moment of 1.77 μ_B at 298 K, but the value for $[Ru_3(py)_3O(CH_3CO_2)_6]^+(ClO_4)^-$ is 2.46 μ_B. In complex $Ru_3(H_2O)_3O(CH_3CO_2)_6$, ruthenium shows an average oxidation state of 2.67, and its low magnetic moment of 0.4 μ_B at 298 K shows all the *d*-electrons to be fully paired. Unfortunately, it was not stated whether the data are values per Ru_3 unit or per ruthenium atom, so it is unclear whether the first compound has 1 unpaired electron on each ion or on each metal atom. In later work (*177*) including π-acceptor ligands, the ruthenium(III) complexes $Ru_3(CH_3OH)_2(SO_2)O(CH_3CO_2)_6(CH_3O)$ and $Ru_3(py)_3(SO_2)O(CH_3CO_2)_7$ showed moments of 2.44 and 2.84 μ_B, respectively, whereas complexes with oxidation state 2.67 ranged in magnetic moment from 1.28 to 2.09 μ_B at room temperature. From NMR spectra (Section VII), some of these compounds are thought to have a variation of the trinuclear structure (Fig. 22). Although this structure contains an Ru_3O triangular core, only 2 of the ruthenium atoms are thought to be bridged



L = MeOH or py

FIG. 22. Proposed structure of $Ru_3L_2(CO)(CH_3CO_2)_6$. [From Spencer and Wilkinson (*177*), by permission.]

by a pair of acetate groups, with the other acetate ions chelating 1 ruthenium atom.

Trinuclear clusters of formula $M_3L_3O(RCO_2)_6$ containing rhodium(III) or iridium(III) all have moments below 1 μ_B (*178*). Two clusters of this type with iridium in oxidation state 3.33 were prepared in this work but their magnetic moments were unfortunately not recorded.

The linear trimer $Co_3(quin)_2(C_6H_5CO_2)_6$ shows surprisingly small antiferromagnetism with a Weiss constant of 19° and a magnetic moment of 4.87 μ_B at 298 K falling to 3.58 μ_B at 98 K (*59*). The 2-nitrobenzoate analog has a moment of 4.80 μ_B at 298 K falling to 4.48 μ_B at 98 K and a Weiss constant of 22° (*154*).

D. OTHER POLYNUCLEAR CARBOXYLATES

The tetranuclear oxopivalate of cobalt(II), $Co_4O(Me_3CCO_2)_6$, has a low room temperature magnetic moment of 3.68 μ_B per cobalt atom (*63*), but data at other temperatures are needed to decide whether the HDVV treatment for 4 equivalent ions of spin 1.5 is appropriate for this molecule.

The cobalt(II)–cobalt(III) tetramer, $Co_4(CH_3CO_2)_2(CH_3O)_4(C_5H_7O_2)_4$ (Fig. 12), has a room temperature magnetic moment of 4.98 μ_B per cobalt(II) atom, assuming the cobalt(III) to be diamagnetic, which decreases to 4.62 μ_B at 77 K. The results were attributed (*64*) to superexchange, but the values are appropriate for noninteracting octahedral cobalt(II) atoms.

The trinucleating ligand, 4-hydroxy-bis-3,5-[*N*-(2′-hydroxyphenyl)-formimidoyl] (H_3L) forms the complex $Co_2L(CH_3O)(CH_3CO_2)$ whose magnetic moment of 3.58 μ_B corresponds to equal proportions of cobalt(II) and cobalt(III) (*66*).

A number of iron(III) carboxylates seem to have clusters of more than 3 metal atoms. Magnetic studies by Kokot *et al.* (*179*) on the series $Fe(RCO_2)(CH_3O)_2$ gave better fits for an Fe_4 square-planar unit than an Fe_4 tetrahedron, an Fe_3 equilateral triangle, or an infinite chain. However, the preference for an Fe_4 square is not at all definite and leads in some cases to the curious result that coupling to an opposite iron atom is stronger than coupling to a neighbor. The room temperature moments are in the range 4.70 to 4.96 μ_B, and J is of the order of $-4\ cm^{-1}$. It is unfortunate that the insolubility of the compounds prevents recrystallization for better magnetic data and crystal structure determination.

The compound $Fe_4(CH_3CO_2)_6(CH_3O)_6$ was shown (*180*) to be tetrameric by ebullioscopy. Its magnetic moment of 4.98 μ_B at 298 K falls to 4.13 μ_B at 98 K, giving a good fit to a tetrahedral cluster of iron atoms with J equal to $-2\ \text{cm}^{-1}$.

Infrared and mass spectra (Sections VI and VIII) (*180*) indicate that $Fe_4O(CH_3CO_2)_{10}$ contains a tetrahedral cluster, and the acetate salt of $[Fe_5O(CH_3CO_2)_{12}]^+$ a trigonal bipyramidal one. The latter compound is antiferromagnetic ($\mu = 3.35\ \mu_B$ at 298 K and 2.36 μ_B at 98 K), but with three variable J values available no curve fitting was attempted. The tetramer is remarkable in being slightly ferromagnetic. Its moment rises from 6.14 μ_B at 298 K to 6.22 μ_B at 123 K, and the Weiss constant has the ferromagnetic value of $-12°$. As the compound is not crystalline, calculations of J values would be premature.

Polymeric carboxylates that are not based on cluster units are excluded from the review, but the most recent studies (*181*, *182*) of the series $VO(RCO_2)_2$ confirm earlier predictions (*183*, *184*) that these are linear chain polymers whose syn-syn bridges (Fig. 23) allow antiferromagnetic interactions to occur ($\mu = 1.25\ \mu_B$ at 293 K and $\sim 0.6\ \mu_B$ at 90 K). The data are best fitted (*181*) by the Ising model of anisotropic exchange that replaces the isotropic spin Hamiltonian,

$$\mathscr{H} = -2J \sum_{i=1}^{n} \mathbf{S}_i \cdot \mathbf{S}_{i+1} \tag{10}$$

by the anisotropic Hamiltonian

$$\mathscr{H} = -2J \sum_{i=1}^{n} \mathbf{S}_i^z \cdot \mathbf{S}_{i+1}^z \tag{11}$$

This leads (*185*) to values of the magnetic moments of

$$\mu_{\|}^2 = 0.75 g^2 e^{2K} \tag{12}$$

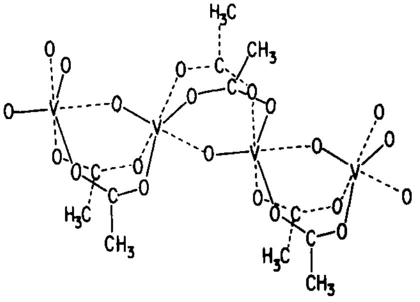


FIG. 23. Proposed structure of $VO(CH_3CO_2)_2$. [From Walter *et al.* (*182*), by permission.]

and

$$\mu_{\perp}^{2} = 0.375g^{2}(\operatorname{sech}^{2} K + K^{-1} \tanh K) \qquad (13)$$

where $K = J/kT$. It would be valuable to measure the single-crystal susceptibilities of these compounds if they could be obtained crystalline. Powder data give J values near $-166\ \text{cm}^{-1}$, but the derived g values are sometimes different from those obtained by EPR spectroscopy.

There remain a few reports that are not sufficiently detailed for reliably deducing structures. The 2,2′-bipyridyl or 1,10-phenanthroline complexes $CrL(H_2O)(CH_3CO_2)(OH)_2$ have low room temperature moments of 3.58 and 3.47 μ_B, respectively, indicating cluster formation (*186*), as do the antiferromagnetic Weiss constants of about 110° found (*187*) for the chromium(III) anthranilate (X) complexes, $(CrX_2Y)_{2n}{\cdot}nH_2O$ ($Y = Cl$ or NO_3), where moments fall from 3.2 to 2.6 μ_B in the liquid nitrogen range.

Compound $Co(CH_3CO_2)(CH_3O)_2$ is believed (*188*) to be polymeric with low-spin cobalt(III). The magnetic moment of 0.75 to 1.74 μ_B, varying with different samples, is attributed to cobalt(II) impurities but may also include some second-order paramagnetism, which is often substantial in low-spin cobalt(III) compounds.

The diamagnetism of the compounds formulated (*189*) as $W_3LO{\cdot}(CH_3CO_2)_8OH$ ($L = H_2O$, CH_3OH) indicated that these had cluster structures, but a later study, using a rather different preparative method, reported (*190*) formation of only $W(CH_3CO_2)_2$. This is also diamagnetic and was believed to be polymeric.

IV. Electron Paramagnetic Resonance Spectroscopy

A. COPPER(II) CARBOXYLATES

Most of the electron paramagnetic resonance (EPR) spectra of polynuclear carboxylates have been obtained from copper(II) compounds, and the results have provided valuable confirmation of the conclusions derived from magnetic susceptibility measurements, with parameters from one experiment often being used to help the interpretation of the other. Investigations up to 1970 are included in a review of EPR studies of exchange-coupled metal ions (*191*) and in a general review of the technique applied to inorganic systems (*192*).

Lancaster and Gordy (*193*) recorded the EPR spectrum of powdered $Cu_2(H_2O)_2(CH_3CO_2)_4$, not then recognized as being dimeric, and realized that it could not be interpreted as arising from a single Cu^{2+} ion in a ^2D ground state in any allowable crystal field. Bleaney and Bowers (*1*), following Guha's report (*81*) of the anomalous temperature dependence of the magnetic susceptibility of copper(II)

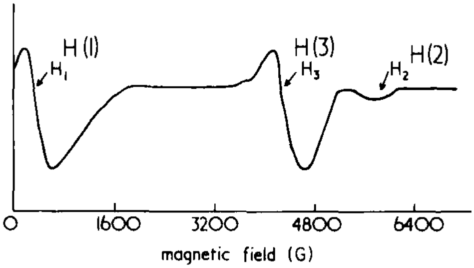


FIG. 24. Electron paramagnetic resonance spectrum of polycrystalline $Cu_2(H_2O)_2(CH_3CO_2)_4$. [From Mabbs and co-workers (*112*), by permission.]

acetate monohydrate, investigated the EPR of a single crystal of the complex and found that this spectrum was also very different from those of normal copper(II) compounds. The spectrum of a polycrystalline sample at room temperature is illustrated in Fig. 24, which is taken from a later report (*112*) because earlier ones did not present the spectrum in the usual derivative form.

The spectrum resembles that of a nickel(II) salt in which the metal ion has a spin of 1. Three transitions are observed, and these become slightly weaker and sharper at 90 K and may show seven-line hyperfine splitting from 2 equivalent copper nuclei with spin $\frac{3}{2}$. At lower temperatures the intensity is further reduced, and no spectrum is seen at 20 K. These observations, coupled with the anomalous susceptibility data, prompted Bleaney and Bowers's hypothesis concerning the coupling of pairs of copper atoms to give a ground singlet state with an excited triplet state whose population varied with temperature. The energy level diagram in Fig. 25 shows the variation in the m_s levels

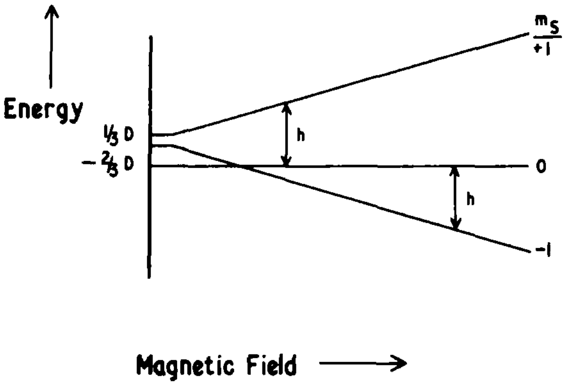


FIG. 25. Spin energy levels in dimeric copper(II) compounds.

with magnetic field. There are two allowed transitions with $\Delta m_s = \pm 1$. The axial symmetry of the molecule causes further splitting. The spin Hamiltonian for the system is

$$\mathscr{H} = D\mathrm{S}_z^2 + E(\mathrm{S}_x^2 - \mathrm{S}_y^2)g_z H_z \mathrm{S}_z + g_x H_x \mathrm{S}_x + g_y H_y \mathrm{S}_y \qquad (14)$$

In many cases g_x and g_y are equivalent, and the spin Hamiltonian becomes

$$\mathscr{H} = D\mathrm{S}_z^2 + g_{||} H_z \mathrm{S}_z + g_{\perp}(H_x \mathrm{S}_x + H_y \mathrm{S}_y) \qquad (15)$$

In these equations, D and E are the tetragonal and rhombic zero-field splitting parameters, and the z axis is taken parallel with the copper–copper direction. The energy levels in the parallel direction are

$$\omega_1 = D + g_{||}\beta H_{||} \qquad (16a)$$

$$\omega_2 = D - g_{||}\beta H_{||} \qquad (16b)$$

$$\omega_3 = 0 \qquad (16c)$$

and in the perpendicular direction,

$$\omega_4 = -0.5D + (0.25D^2 + g_{\perp}^2\beta^2 H_{\perp}^2)^{1/2} \qquad (17a)$$

$$\omega_5 = -0.5D - (0.25D^2 + g_{\perp}^2\beta^2 H_{\perp}^2)^{1/2} \qquad (17b)$$

$$\omega_6 = 0 \qquad (17c)$$

At X-band frequencies, three transitions are seen:

$$h\nu = D - g_{||}\beta H_1 \qquad (18a)$$

$$h\nu = -D + g_{||}\beta H_2 \qquad (18b)$$

$$h\nu = -0.5D + (0.25D^2 + g_{\perp}^2\beta^2 H_3^2)^{1/2} \qquad (18c)$$

These transitions are identified in Fig. 24. At 90 K, Bleaney and Bowers derived the values $D = 0.34 \pm 0.03\ \mathrm{cm}^{-1}$, $E = 0.01 \pm 0.005\ \mathrm{cm}^{-1}$, $g_{||} = 2.42 \pm 0.03$, and $g_{\perp} = 2.08 \pm 0.03$. By comparing the intensity of one of the narrow lines of the dimer's spectrum with that of a normal nickel(II) compound over the range 60–90 K, the singlet–triplet separation was estimated to be $315\ \mathrm{cm}^{-1} \pm 20\%$. The accuracy was limited by the changing line width. A correction was made for this, but the value does agree reasonably well with the value of $-2J$ found from the susceptibility data.

Electron paramagnetic resonance spectra have been obtained for many copper(II) carboxylates and the results for those showing copper–copper interactions are given in Table VI. Most of the experiments require no further discussion; only results of particular significance will be mentioned.

A value of 0.345 cm^{-1} for D in $Cu_2(CH_3CO_2)_4(urea)_2(H_2O)_2$ was taken to indicate coordination by urea rather than water, but the values in Table VI do not indicate a sharp variation with the axial ligand, and this conclusion may not be justified (*213*). Compounds of the type $Cu_2L_2(RCO_2)_2(R'CO_2)_2$ gave similar spectra to those containing identical carboxylate groups, and no attempt was made to distinguish possible geometrical isomers (*197*).

The EPR spectra of zinc-doped $Cu_2(H_2O)_2(CH_3CO_2)_4$ (*214*) and $Cu_2(ClCH_2CO_2)_4$ (*200*) with a Cu/Zn ratio of about 200:1 showed additional peaks from species of spin $\frac{1}{2}$. In the mixed dimers the diamagnetic zinc ions prevent the exchange interaction, giving a "normal" copper spectrum. The hyperfine coupling constants from the spectra due to Cu—Zn pairs were about double those in the Cu_2 spectra, but the g values were the same, suggesting that the copper ions are only weakly coupled.

A particularly valuable result of EPR experiments on polycrystalline copper(II) carboxylates has been the detection of magnetically dilute copper(II) impurities in samples that were analytically pure (*112, 206–208, 215*). The intensity of the signal from the impurity increases as the temperature falls, in contrast to the resonances due to the triplet state of the dimer, which decrease at lower temperature. Also, where hyperfine coupling is resolved, four lines are found with a coupling constant about double that of the triplet species. One study (*207*) of copper(II) benzoate has shown that the allegedly different modifications of this compound, postulated to explain magnetic susceptibility data, are simply a dimeric structure with varying degrees of impurity.

Cyclic bidentate ligands, such as pyrazine or dioxane, form complexes with copper(II) carboxylates in which 1 molecule of ligand bridges two dimer units and a polymeric structure results with the formula $Cu_2(bi)(RCO_2)_4$ (Fig. 26). There is now the possibility of magnetic exchange through the bridging pyrazine ligand, but the EPR spectra indicate that this gives an additional J of about 0.1 cm^{-1}, much smaller than the exchange between the copper atoms bridged by acetate groups (*198*). In this work it was concluded that the separation of the copper atoms in copper(II) acetate was at least 0.1 Å greater in the triplet state than in the singlet state.

TABLE VI

ELECTRON PARAMAGNETIC RESONANCE PARAMETERS FOR ANTIFERROMAGNETIC COPPER(II) CARBOXYLATES $[CuL(RCO_2)_2]$

R[a]	L[b]	D (cm^{-1})	E (cm^{-1})	g_x	g_y	g_z	Ref.
CH_3	H_2O	0.34	—	2.08	2.08	2.35	(*112*)
CH_3	H_2O	0.34	0.01	2.08	2.08	2.42	(*83*)
CH_3	H_2O	0.34	0.007	2.05	2.09	2.34	(*194*)
CH_3	Py	0.340	≤0.003	2.065	2.070	2.362	(*195*)
CH_3	Quin	0.341	0.002	2.06	2.06	2.37	(*196*)
CH_3	Quin	0.348	≤0.001	2.067	2.070	2.365	(*195*)
CH_3	Nqun	0.343	0.0006	2.07	2.07	2.37	(*197*)
CH_3	$\frac{1}{2}$ Pyz	0.33	<0.01	2.09	2.09	2.37	(*198*)
CH_3	Antipy	0.346	—	2.053	2.053	2.348	(*96*)
FCH_2	Quin	0.395	0.002	2.09	2.09	2.40	(*197*)
FCH_2	Pdp	0.386	—	2.05	2.05	2.38	(*199*)
$ClCH_2$	—	0.342	—	2.07	2.07	2.38	(*200*)
$ClCH_2$	Nqun	0.370	0.001	2.07	2.07	2.38	(*197*)
$ClCH_2$	Pdp	0.365	—	2.05	2.05	2.42	(*199*)
$BrCH_2$	Pdp	0.360	—	2.05	2.05	2.42	(*199*)
ICH_2	—	0.333	—	2.12	2.12	2.36	(*201*)
ICH_2	$\frac{1}{2}$ Diox	0.329	—	2.11	2.11	2.36	(*201*)
ICH_2	Pdp	0.340	—	2.06	2.06	2.40	(*199*)
C_2H_5	H_2O	—	—	2.09	2.09	2.34	(*202*)
C_2H_5	H_2O	0.327	—	2.06	2.06	2.35	(*200*)
CH_3CHF	$\frac{1}{2}$ Diox	—	—	2.112	2.112	2.395	(*93*)
CH_3CHCl	—	0.337	0.004	2.056	2.056	2.339	(*203*)
CH_3CHBr	—	0.340	0.011	2.060	2.060	2.341	(*203*)
CH_3CCl_2	—	0.354	—	2.09	2.09	2.38	(*201*)
CH_3CCl_2	$\frac{1}{2}$ Diox	0.357	—	2.09	2.09	2.38	(*201*)
BrC_2H_4	H_2O	0.342	—	2.063	2.063	2.308	(*203*)
IC_2H_4	—	0.340	—	2.03	2.03	2.38	(*201*)
IC_2H_4	$\frac{1}{2}$ Diox	0.340	—	2.08	2.08	2.34	(*201*)
C_3H_7	H_2O	0.333	0.011	2.06	2.06	2.34	(*204*)
$NCCH_2$	—	0.39	—	2.08	2.08	2.40	(*205*)
C_6H_5	—	0.331	0.015	2.05	2.07	2.34	(*206*)
C_6H_5	$2CH_3OH$	0.330	0.004	2.051	2.051	2.342	(*207*)
C_6H_5	$C_2H_5OH + H_2O$	0.334	0.003	2.067	2.067	2.356	(*207*)
C_6H_5	Diox + H_2O	0.332	0.003	2.051	2.051	2.342	(*207*)
C_6H_5	2 Acetone	0.335	0.003	2.064	2.064	2.352	(*207*)
C_6H_5	2 Mek	0.337	0.003	2.061	2.061	2.352	(*207*)
C_6H_5	Py	0.357	—	2.07	2.07	2.37	(*208*)
C_6H_5	Quin	0.34	—	2.07	2.07	2.32	(*112*)
C_6H_5	Antipy	0.371	—	2.068	2.068	2.357	(*96*)
2-$CH_3C_6H_4$	—	0.34	—	2.07	2.07	2.34	(*112*)
2-$CH_3C_6H_4$	Py	0.37	—	2.07	2.07	2.37	(*208*)
2-$NO_2C_6H_4$	—	0.36	—	2.05	2.05	2.38	(*112*)
2-$NO_2C_6H_4$	—	0.36	0.037	2.06	2.06	2.39	(*208*)
2-$NO_2C_6H_4$	H_2O	0.35	—	2.05	2.05	2.35	(*112*)
2-$NO_2C_6H_4$	Py	0.38	—	2.07	2.07	2.37	(*208*)

TABLE VI—*Continued*

R[a]	L[b]	D (cm^{-1})	E (cm^{-1})	g_x	g_y	g_z	Ref.
2-BrC_6H_4	H_2O	0.34	—	2.06	2.06	2.34	(*112*)
2-IC_6H_4	—	0.35	—	2.06	2.06	2.34	(*112*)
2-OHC_6H_4	Antipy	0.357	—	2.073	2.073	2.376	(*96*)
3-$CH_3C_6H_4$	—	0.33	—	2.07	2.07	2.36	(*208*)
4-ClC_6H_4	—	0.34	—	2.06	2.06	2.36	(*112*)
4-OHC_6H_4	3 Diox	0.292	0.003	2.044	2.044	—	(*209*)
4-OHC_6H_4	3 DMF	0.302	0.001	2.038	2.038	—	(*209*)
4-OHC_6H_4	3 DMSO	0.603	0.002	2.476	2.476	—	(*209*)
4-OHC_6H_4	3 Quin O	0.378	—	2.160	2.160	—	(*209*)
2,4-$Cl_2C_6H_3$	—	0.35	—	2.07	2.07	2.32	(*112*)
1-Naphth	H_2O	0.34	—	2.07	2.07	2.35	(*112*)
1-Naphth	Py	0.37	—	2.07	2.07	2.38	(*112*)
o-Cres	Antipy	0.355	—	2.084	2.084	2.376	(*96*)
m-Cres	Antipy	0.346	—	2.079	2.079	2.351	(*96*)
p-Cres	Antipy	0.347	—	2.055	2.055	2.339	(*96*)
2-Furan	H_2O	0.353	0.004	2.058	2.058	2.356	(*210*)
2-Thiophen	H_2O	0.337	0.004	2.064	2.064	2.358	(*211*)
$ClCH_2$	$C_6H_5NH_2$	0.124	—	2.06	2.06	2.34	(*212*)
C_2H_5	$C_6H_5NH_2$	0.129	—	2.06	2.06	2.36	(*212*)
C_2H_5	3-$CH_3C_6H_4NH_2$	0.136	—	2.05	2.05	2.34	(*212*)
C_2H_5	4-$CH_3C_6H_4NH_2$	0.131	—	2.04	2.04	2.37	(*212*)
C_3H_7	$C_6H_5NH_2$	0.133	—	2.06	2.06	2.34	(*212*)

[a] Abbreviations: Naphth = naphthoate; Cres = cresotate; 2-Furan = furan 2-carboxylate; 2-Thiophen = thiophen 2-carboxylate.

[b] Abbreviations: Py = pyridine; Quin = quinoline; Nqun = β-naphthoquinoline; Pyz = pyrazine; Antipy = antipyrine; Pdp = 1-phenyl-2,3-dimethyl-5-pyrazolone; Diox = dioxane; Mek = 2-butanone; Quin O = quinoline *N*-oxide.

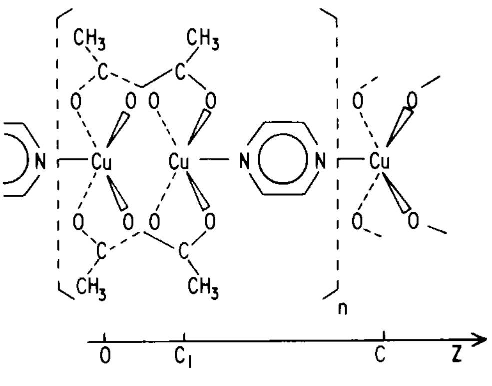


FIG. 26. Proposed structure of polymeric $Cu(C_4H_4N_2)(CH_3CO_2)_2$. [After Valentine *et al.* (*198*). Reproduced with permission from *J. Amer. Chem. Soc.* **96**, 97 (1974). Copyright by the American Chemical Society.]

Despite the crystallographic evidence (Section II,E) that anilines form polymeric complexes with copper(II) carboxylates, even though the formula is $[CuL(RCO_2)_2]$, the observation of an EPR spectrum of a triplet state for these compounds led to the conclusion that they were dimers (*212*). To fit the data, an additional parameter was invoked (*216*) and assigned the role of representing intermolecular exchange between dimers.

B. CARBOXYLATES OF OTHER METALS

There have been very few investigations of the EPR spectra of carboxylate clusters involving metals other than copper. The spectra of the polymeric $[VO(RCO_2)_2]$ compounds consist of a single, broad symmetric absorption (*181*). No hyperfine structure due to coupling with the ^{51}V nucleus ($I = 7/2$) was observed over the temperature range 77–300 K. This behavior is characteristic of relaxation arising from strong intermolecular interactions and supports the proposed polymeric structure. The vanadium(III) dimers, $(C_5H_5)_2V_2(RCO_2)_4$ and $(C_5H_5)_4V_2(C_6H_5CO_2)_4$ and the titanium(III) compound, $(C_5H_5)_2Ti_2(C_6H_5CO_2)_4$, all have spectra corresponding to a triplet-spin state (*148*, *217*). A single crystal of the cobalt(II) dimer, $Co_2(quin)_2(C_6H_5CO_2)_4$, shows a very complex EPR spectrum at 20 K, indicating hyperfine coupling to both ^{59}Co and ^{14}N ($I = 7/2$ and 1, respectively) (*151*).

There are a few reports of spectra from the trinuclear cations $[M_3L_3O(RCO_2)_6]^+$. For M = Cr, values of g from 1.89 to 1.95 were obtained (*218*) and the zero-field splitting calculated. However, the work assumed inequivalent values of the J parameters, which, according to electronic spectra and heat capacity measurements (Sections V,C and X), have been shown to be inappropriate. For $M_3 = Cr_2Fe$ or $CrFe_2$, the value of g was 1.95 and the magnitudes of the J parameters were in the order $J(Fe—Fe) > J(Fe—Cr) > J(Cr—Cr)$ (*219*, *220*).

V. Electronic Spectroscopy

As electronic spectra are very easy to measure, there have been many reports of data of this kind for carboxylate clusters. This section only deals with compounds for which the spectrum of the cluster shows differences from that of a similar monomer.

A. DIMERIC COPPER(II) CARBOXYLATES

The story of the measurement and elucidation of the electronic spectrum of copper(II) acetate is particularly instructive in showing progress in the study of this technique. The earliest report was of a

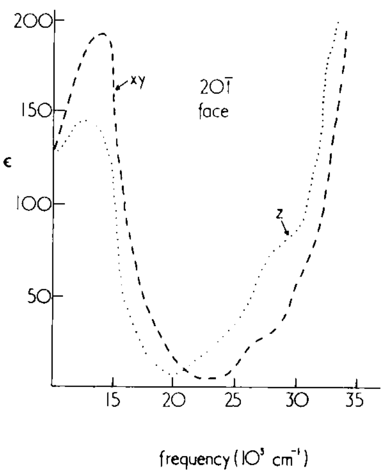


FIG. 27. Polarized single-crystal spectrum of $Cu_2(H_2O)_2(CH_3CO_2)_4$. [After Ross and co-workers (*228*), by permission.]

polarized spectrum of a single crystal of $Cu_2(H_2O)_2(CH_3CO_2)_4$ (*221*). The two well-defined absorption bands are shown in Fig. 27.

Band I, at about 14,300 cm^{-1}, was polarized in the plane of the oxygen atoms (*xy* plane) and was considered to be the "ordinary copper(II) band," but band II, at about 27,000 cm^{-1}, was polarized along the copper–copper axis (*z* direction) and is not usually seen in the spectra of octahedral copper(II) compounds. The polarized electronic spectrum of $[Cu(H_2O)(C_2H_5CO_2)_2]$ resembled that of the acetate, but $Cu(H_2O)_4(HCO_2)_2$, which was known to be polymeric (71), showed only band I. Thus, in later work (*222–224*), the appearance of band II was taken to be diagnostic of a dimeric structure, but since then a number of nondimeric copper(II) compounds have been found to exhibit band II. Such compounds include copper(II) ethylacetoacetate (*225*) and other probably planar monomeric species (*226*) and the polymeric 4-toluidine adduct of $Cu(C_2H_5CO_2)_2$ (*72*).

It is not necessary to list all the measurements on dimeric copper(II) carboxylates and their adducts, as these are so similar, but it has been found that the position and intensity of band I are sensitive to the nature of the axial ligand, whereas those of band II are not. Band II is often hard to locate accurately as it may occur as a shoulder on a stronger charge-transfer band.

The next stage in the investigation of these spectra was their resolution into three Gaussian components at 11,000 (Ia), 14,000 (Ib), and 27,000 cm^{-1} (II) (*227*). Band Ia was particularly sensitive to the change of the axial ligand, moving to lower energy as the donating power of the axial ligand increased. A very intense band (band III) at 40,000 cm^{-1} was also observed, and this was sensitive, not to variations in the axial ligand, but to changes in the alkanoate ion. Further investigation of the single-crystal spectrum of $Cu_2(H_2O)_2(CH_3CO_2)_4$ showed band III as a very broad and intense absorption over the range 30,000–50,000 cm^{-1} (*228*). Band Ia was also recognized as a shoulder on band Ib, was z-polarized like band II, and became more pronounced at liquid nitrogen temperature (*229*).

The origin of these bands has been a topic of great discussion. The very intense band III was assigned (*227*) as a ligand to metal charge-transfer band. Using simple molecular orbital theory, band II was concluded to be a transition between orbitals associated with a σ bond between the copper atoms. Tonnet *et al.* (*228*) favored a valence bond approach leading to a copper–copper δ bond but did not make a specific assignment. By comparing the EPR spectrum of pure and zinc-doped $Cu_2(H_2O)_2(CH_3CO_2)_4$ (Section IV,A), Kokoszka and Allen (*214*) concluded that a weakly coupled chromophore model gave a better description of the copper–copper interaction. The energy levels can then be described in terms of a single tetragonally distorted Cu^{2+} ion and transitions will be from lower orbitals to the $d_{x^2-y^2}$ orbital. Reimann *et al.* (*229*) considered the observed polarization of the bands in terms of the requirements of the possible point groups, shown in Table VII. As band Ib is xy-polarized, it could be assigned to a $d_{xz,yz} \rightarrow d_{x^2-y^2}$ transition, whereas band Ia, being z-polarized, could be due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition. The origin of band II was not established, but if it were a d–d band, it could be assigned to a $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. If this band is not a d–d transition, then band Ia may be the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. However, Hansen and Ballhausen

TABLE VII

POLARIZATION OF ELECTRONIC TRANSITIONS IN $Cu_2(H_2O)_2(CH_3CO_2)_4$

	Point group		
Transition	C_{4v}	C_{2v}	C_2
$z^2 \rightarrow x^2 - y^2$	—	z	z
$xy \rightarrow x^2 - y^2$	—	—	z
$xz \rightarrow x^2 - y^2$	x, y	x	x, y
$yz \rightarrow x^2 - y^2$	x, y	y	x, y

(*230*) suggested that band II was due to a transition to a doubly excited state of the type $(d_{z^2} \rightarrow d_{x^2-y^2})^2$.

Later developments in this problem have come from Dubicki and Martin. They found (*132*) that on varying the axial ligand, band Ib shifted to higher energy as the ligand became more electron-withdrawing, but band II shifted to lower energy, and so appeared to be a charge-transfer transition and not a *d–d* transition. As the methyl groups of the acetate bridges were substituted with chlorine atoms, band I as expected shifted to lower energy as the ligand field strength decreased, but band II shifted to higher energy, again favoring a charge-transfer assignment.

A reexamination of the crystal spectrum of $Cu_2(H_2O)_2(CH_3CO_2)_4$ under higher resolution over the temperature range 4.2–290 K showed that band II had two components, at 27,800 (IIa) and 30,800 cm^{-1} (IIb), that are *z*- and *xy*-polarized, respectively (*231*). The intensity of the IIa component doubled in the temperature range 287–77 K, but changed little between 77 and 4.2 K. This indicated that the band originates from the singlet ground state of the dimer, as the population of this state would increase from about 57% at 290 K to 99% at 77 K, and then change little between 77 and 4.2 K. However, the intensity of band I only increases by 10 to 15% between 290 and 77 K, so that the singlet and triplet *d–d* transitions must be superimposed. The intensity measurements of band IIb were less conclusive, but it was considered to be a charge-transfer band like band IIa.

B. OTHER DIMERIC CARBOXYLATES

The visible spectrum of $Cr_2(H_2O)_2(CH_3CO_2)_4$ is characterized by an unusually broad band centered at 20,800 cm^{-1}, which is probably a composite of several bands (*132*). Since the singlet-spin state lies lowest by about 700 cm^{-1} (*83*) (Section III,B), most of the molecules will be in this state at room temperature and the spectrum will consist of singlet–singlet transitions at similar frequencies to the quintet–quintet and quintet–singlet transitions of monomeric high-spin chromium(II) species. The ultraviolet spectrum consists of a broad absorption between 34,500 and 48,000 cm^{-1}, with a relatively sharp shoulder at 30,700 cm^{-1}. These are all assigned as charge-transfer bands.

The electronic spectra of the binuclear molybdenum(II) carboxylates show a weak absorption at about 23,000 cm^{-1} (band I) and a strong absorption in the region 20,000–35,000 cm^{-1} (band II) (*232*). Band I exhibits vibrational fine structure, which is clearly resolved at 77 K.

Band II, which consists of an intense component with shoulders lying at lower energy, was tentatively assigned as a 1-electron metal–metal transition.

The reflectance spectra of $Co_2(quin)_2(RCO_2)_4$, where R = C_6H_5 or 2-$O_2N \cdot C_6H_4$, resemble that of the square pyramidally coordinated Co^{2+} ion in $[Co(Ph_2MeAsO)_4(ClO_4)]^+ (ClO_4)^-$ (*233*), but no new transitions were seen and the bands could be assigned on a model for an isolated high-spin Co^{2+} ion in the C_{4v} point group (*154*).

The reflectance spectrum of $Rh_2(CH_3CO_2)_4$ shows bands at 16,200 and 22,600 cm^{-1} (*234*). The spectra of several adducts of rhodium(II) acetate indicate that the low-energy band is very sensitive to the nature of the terminal ligands, but the high-energy band is relatively insensitive (*235*, *236*). Somewhat similar results are found in the probably dimeric compounds $[Rh(RCO_2)XY]$, where X is a diketonate group, and Y a neutral ligand (*237*). The structures of these compounds are discussed in Section VII.

The electronic spectra of the rhenium(III) carboxylate monohalide complexes exhibit several bands that could not be assigned in any detail (*238*). For the series of complexes $Re_2X_2(C_3H_7CO_2)_4$, where X = Cl, Br, and I, a very intense band in the near-ultraviolet region was observed to decrease in energy in the order Cl > Br > I. It was suggested that this order reflected the weakening of the Re—Re bond.

C. OTHER CARBOXYLATE CLUSTERS

The visible spectra of the chromium(III) basic acetates (Fig. 28) form an excellent example of the spectrum of a Cr^{3+} ion in a tetragonal field (*239*).

The shoulder at 15,100 cm^{-1} was assigned as a transition to the $^4B_2$ component of the $^4T_{2g}$ octahedral state, and the intense band at 16,900 cm^{-1} was assigned as a transition to the ^4E component (Fig. 29). The higher-energy intense band at about 22,200 cm^{-1} was thought to be due to transitions to the ^4E and $^4A_2$ components of the $^4T_{1g}(F)$ state, but no splitting was observed. The unusual weak ultraviolet absorption bands were considered to be spin-forbidden bands.

A high-resolution polarized spectrum of a single crystal of the complex $[Cr_3(H_2O)_3O(CH_3CO_2)_6]^+Cl^- \cdot 6H_2O$ was measured over the temperature range 300–4.2 K in order to study the temperature dependence of the bands' intensities (*240*). The band at 16,900 cm^{-1} was split into two components at 16,700 and 17,400 cm^{-1}, which were polarized in different directions and assigned as transitions to the

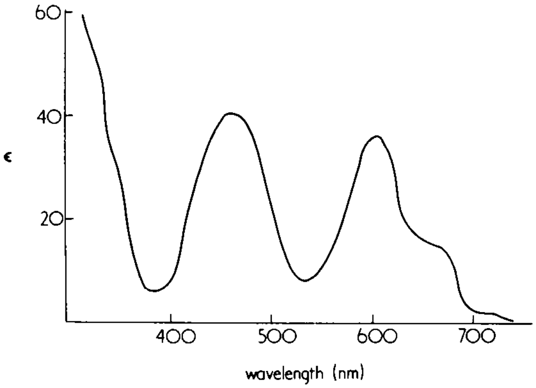


FIG. 28. Electronic spectrum of $[Cr_3(H_2O)_3O(CH_3CO_2)_6]^+$ in methanol. [From Dubicki and Martin (*239*), by permission.]

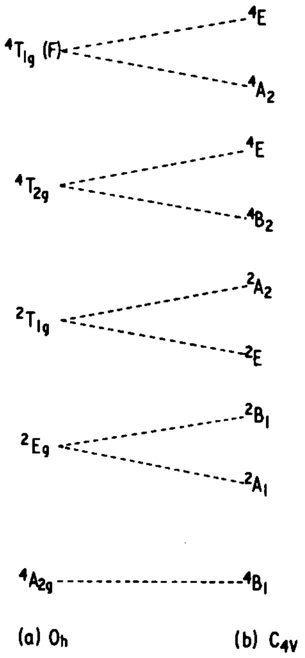


FIG. 29. Energy levels of Cr^{3+} ions in O_h or D_{4h} symmetry.

$^4B_2$ and ^4E tetragonal components of the $^4T_{2g}$ octahedral level, respectively. The absorption at 15,000 cm^{-1} was now considered to be a spin-forbidden $^4B_1 \rightarrow {}^2A_2({}^2T_{1g})$ transition. Some low-energy absorption over the range 14,500–13,300 cm^{-1} was resolved into several components, which were thought to contain spin-forbidden transitions corresponding to $^4A_{2g} \rightarrow {}^2E_1, {}^2T_{1g}$ in regular octahedral complexes. The temperature dependence of the intensities of these bands indicated that they are dominated by the components originating in the ground-state singlet level of the exchange-split $^4B_1$ state. The fine structure of the near-ultraviolet spectrum was well resolved into a set of sharp absorption bands, assigned as double excitations of the $^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$ transitions, which become allowed by the exchange interaction.

The latest information on this cluster came from a study (*241*) of the luminescence and luminescence excitation spectra at 7 K. In the range 12,800–13,500 cm^{-1}, it was possible to observe all the components of the formally quartet-doublet transitions and, thus, calculate the separations of the various spin-energy levels in the ground and excited states. The ground-state spin levels are $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, and $\frac{9}{2}$, but those of the excited state are $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, and $\frac{7}{2}$. It was also possible to detect a lifting of the degeneracy of some spin levels by allowing for different values of J [see Eq. (9), Section III,C]. After this thorough analysis, it was found that the observed spectrum was really the superposition of two spectra from slightly inequivalent clusters, although this inequivalence has not been detected crystallographically. For one cluster, $J = -21.5$ cm^{-1} and $J' = -24.6$ cm^{-1}, and for the other, $J = -21$ cm^{-1} and $J' = -20$ cm^{-1}. The authors indicate that three different J values might be needed to describe the interactions in a triangular cluster, but this has not yet been necessary.

Diffuse reflectance spectra of trinuclear iron(III) basic carboxylates have been recorded but are poorly resolved (*239*). High-spin Fe^{3+} complexes normally show only weak spin-forbidden *d–d* bands, and the charge-transfer absorption usually extends into the visible region, thus obscuring many of the ligand field bands. Mull and solution spectra showed similar features to the reflectance spectra (*167*).

Studies of other triangular carboxylate clusters have often simply used the electronic spectra as "fingerprints" without attempting detailed analysis, but the spectra of some ruthenium (*176*) and iridium (*178*) compounds containing nonintegral oxidation states show significant differences from those of clusters of metals in integral oxidation states and might reward closer study. However, the spectrum of $Co_3(CH_3CO_2H)_3O(CH_3CO_2)_6$ shows bands due to Co^{3+} transitions only (*175*).

The linear trimer $Co_3(quin)_2(C_6H_5CO_2)_6$ contains two tetrahedral and one octahedral environment round Co^{2+} ions. The CoO_3N chromophore dominates the spectrum, but the inequivalent ligands give rise to some differences from the spectra of regular tetrahedral cobalt(II) complexes (*154*). A similar effect was seen in the tetranuclear $Co_4O(Me_3CCO_2)_6$ (*63*).

Among polymeric carboxylates, temperature dependence studies of the solid state absorption spectrum of oxovanadium(IV) acetate and halogenoacetates indicate that the order of d orbitals is $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$ in C_s symmetry. Charge-transfer bands appear above 30,000 cm^{-1} (*182*). There is also a brief report of the reflectance spectrum of tungsten(II) acetate. It resembles that of $Mo_2(CH_3CO_2)_4$, but the mass spectrum (Section VIII) suggests the compound is polymeric (*242*).

VI. Vibrational Spectra

When a ligand coordinates to a metal, its symmetry is usually lowered and many infrared and Raman active vibrations that are degenerate in the spectrum of the free ligand are split in the spectrum of the complex. Thus, a study of the vibrational spectra can often yield useful information about the symmetry and structure of a complex.

Besides bridging 2 metal atoms, a carboxylate group can also act as an uncoordinated anion, a monodentate ligand, or a bidentate chelate, as shown in Fig. 30. In fact, these categories are not sharply distinct. It can be difficult to decide whether or not a ligand is coordinated, and in a few compounds the 2 oxygen atoms of a bidentate carboxylate group may be at different distances from the metal ion, giving unsymmetrical coordination leading in the limit to a monodentate configuration. Nevertheless, the simple classification is a useful working model.

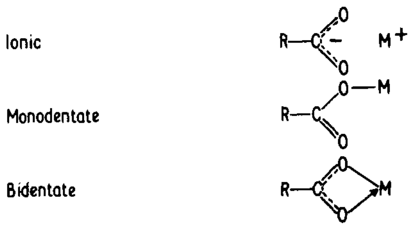


FIG. 30. The three nonbridging types of carboxylate coordination.

Although, in principle, infrared and Raman spectra could be used to distinguish the various configurations, the symmetry of the free carboxylate ion is so low (C_{2v}) that the desirable splitting of degenerate modes does not occur and the assignment of structures from vibrational spectra becomes more difficult. It can be seen that the symmetry of a bidentate or bridging carboxylate group is C_{2v} (ignoring the nature of the group R), the same symmetry as the free ion, so that the same selection rules apply, with all vibrations being allowed in the infrared except A_2 and all in the Raman except A_1. When acting as a monodentate ligand, the carboxylate has C_s symmetry, with all modes allowed in both the infrared and Raman spectra.

The infrared spectrum of sodium acetate has been studied in detail (*243*), and the assignments of the band are given in Table VIII. The most useful bands are the intense antisymmetric carboxylate stretch at 1578 cm^{-1} and the symmetric stretch at 1414 cm^{-1}, which are separated by 164 cm^{-1}. Trends in the positions of and separations between these bands are the most useful observations in assigning structures from infrared spectra.

The CO_2-stretching modes are usually the most prominent features in the infrared spectrum, but some difficulty in assignment can occur in arylcarboxylates, in which the C—H in-plane vibrations of the

TABLE VIII

INFRARED SPECTRA OF SODIUM ACETATE AND COPPER(II) ACETATE

Assignment	Symmetry	Sodium[a,b]	Copper(II)[a,c]
CH_3 antisymmetric stretches	B_2, B_1	2989(w)	2985(w)
CH_3 symmetric stretch	A_1	2935(w)	2938(w)
CO_2 antisymmetric stretch	B_1	1578(s)	1591(s)
CH_3 antisymmetric bend	B_2	1498(w)	—
CH_3 antisymmetric bend	B_1	1443(w)	1440(sh)
CH_3 symmetric bend	A_1	1430(sh)	1352(w)
CO_2 symmetric stretch	A_1	1414(vs)	1420(vs)
CH_3 rock	B_2	1042(m)	1052(m)
CH_3 rock	B_1	1009(m)	1041(m)
CC stretch	A_1	924(w)	958(w)
CO_2 symmetric bend	A_1	646(m)	698(m)
CO_2 rock	B_2	615(m)	627(m)
CO_2 rock	B_1	465(m)	—

[a] Abbreviations: m = medium; s = strong; sh = shoulder; vs = very strong; w = weak.

[b] Data from Ito and Bernstein (*243*).

[c] Data from Costa *et al.* (*244*).

benzene ring occur in the same region as the CO_2 stretches. Also, an investigation (*245*) of the infrared spectra of several sodium salts of substituted acetates showed that the separation between the two carboxylate stretches is very dependent on the nature of the substituent. The results also indicated that the band at about 1400 cm^{-1}, which is usually designated as the symmetric carboxylate stretch, is, in fact, due to mixing of the C—O with the C—C symmetric stretching modes. However, this seems not to detract from the usefulness of the spectra. The alkyl C—H bending modes are also found in this region of the spectrum, but these are generally weak and can easily be distinguished. When the complex contains other ligands beside carboxylate, overlapping bands from the new ligands often make the assignment of the CO_2-stretching frequencies difficult.

In monodentate coordination, the C—O bonds become inequivalent. The antisymmetric stretching frequency increases from its free ion value as the vibration takes on more ketonic character, whereas the symmetric frequency decreases. Hence, a large splitting of the CO_2-stretching frequencies is often an indication of monodentate coordination. Thus, the separation of the two frequencies in $[Co(NH_3)_5CH_3CO_2](ClO_4)_2$ is 223 cm^{-1} (*246*).

Although a large splitting of the carboxylate-stretching frequencies is usually characteristic of a monodentate configuration, a smaller splitting does not exclude this possibility. In $Ni(H_2O)_4(CH_3CO_2)_2$, whose X-ray structural analysis shows both acetates to be monodentate(*247*), the carboxylate-stretching frequencies occur at 1520 and 1413 cm^{-1} (separation, 107 cm^{-1}) (*248*). This small separation is attributed to the strong intramolecular hydrogen bonding between the uncoordinated carboxylate oxygen atom and a water molecule (O—O distance, 2.619 Å). This tends to equate the two C—O bonds and compensates for the asymmetry produced by the monodentate coordination. There is also intermolecular hydrogen bonding between both the carboxylate oxygen atoms and water molecules coordinated to other nickel atoms.

At stated previously, the carboxylate group retains C_{2v} symmetry when acting as a bridging group or as a bidentate chelate and, therefore, from a symmetry viewpoint, the CO_2-stretching frequencies are not expected to be greatly different from the free ion spectrum, although there is likely to be some shifting from having a heavy atom attached to each oxygen. In practice, such changes are very small and cannot be used to establish coordination or to distinguish between bridging and chelate configurations.

Despite the overlap of the ranges of the CO_2-stretching frequencies for different types of carboxylate coordination, some workers have used these bands for structure assignment. One of the more careful studies is that by Curtis (*249*), who compared the infrared spectra of a group of acetato-amine complexes of divalent nickel, copper, and zinc. Because the separation of the carboxylate-stretching frequencies in $[Ni(en)_2(CH_3CO_2)]ClO_4$ (95 cm^{-1}) and the isostructural Zn compound (125 cm^{-1}) was less than the free ion value (164 cm^{-1}), these two compounds were considered to have pseudo-octahedral structures with chelating acetates, although a binuclear structure with 2 bridging acetate groups would also satisfy the data.

Using information from solution and solid state spectra, Lever and Ogden (*250*) assigned the bridging and bidentate, antisymmetric CO_2-stretching frequencies for a series of cobalt(II) and nickel(II) haloacetate complexes $M(py)_n(RCO_2)_2$, where $n = 2$ or 4 and R = CH_2Cl, $CHCl_2$, CCl_3, CH_2F, CHF_2, or CF_3. In solution in chloroform, the bispyridine complexes showed two antisymmetric stretches that were concentration-dependent. The lower-energy band (1640 cm^{-1}) increased in intensity on dilution, whereas the higher-energy band (1680 cm^{-1}), which also occurs in the solid state spectra, decreases in intensity on dilution. These bands were thought to represent chelating and bridging configurations, respectively, but these complexes almost certainly lose pyridine in solution, which will introduce bands for $[Copy(RCO_2)_2]$ or $[Co(RCO_2)_2]$. The separation of 356 cm^{-1} found in $Ni(py)_2(CF_3CO_2)_2$ is the largest claimed for a bidentate carboxylate.

The infrared spectrum of copper(II) acetate is assigned in Table VIII (*244*). In this and for other copper(II)-unsubstituted alkanoates (*222*), there is a sharp, well-defined antisymmetric stretch between 1605 and 1590 cm^{-1}, which at that time was considered diagnostic of a binuclear structure. However, the list of CO_2-stretching frequencies for a selection of cluster carboxylates in Table IX shows that the antisymmetric stretch varies appreciably in energy as different metals are coordinated. The symmetric stretching frequency is usually not shifted far from the free ion value. Not all the compounds in Table IX have been subjected to X-ray analysis, but there is evidence that all have some form of cluster in their molecular structures.

As the data in Table IX indicate, the positions of the CO_2-stretching frequencies may each be anywhere in a range of about 180 cm^{-1} and their separation may be as small as 80 cm^{-1} or over 200 cm^{-1} within the bridging configuration. Therefore, it is hazardous to use infrared spectroscopy alone to assign a cluster structure, and magnetic or EPR data are better criteria when appropriate metal ions are present. Nevertheless, this hazard is often risked.

TABLE IX

Carboxylate-Stretching Frequencies in Polynuclear Carboxylates

Compound[a]	Antisymmetric stretch (cm^{-1})	Symmetric stretch (cm^{-1})	$\Delta\nu$ (cm^{-1})	Ref.
$Cu_2(CH_3CO_2)_4$	1591	1420	171	(*244*)
$Cu_2(H_2O)_2(CH_3CO_2)_4$	1603	1418	185	(*251*)
$Cu_2(pdp)_2(BrCH_2CO_2)_4$	1630	1418	212	(*199*)
$[Cu_2(H_2O)_2(fur)_4]\cdot 4H_2O$	1615	1419	196	(*199*)
$Cr_2(CH_3CO_2)_4$	1571	1422	149	(*244*)
$Cr_2(H_2O)_2(CH_3CO_2)_4$	1575	1420	155	(*251*)
$V_2(CH_3CO_2)_6$	1652, 1612	1431	181, 221	(*146*)
$V_2(C_6H_5CO_2)_6$	1644, 1605	1390	215, 254	(*146*)
$Rh_2(CH_3CO_2)_4$	1588	1433	155	(*235*)
$Rh_2(H_2O)_2(CH_3CO_2)_4$	1580	1430	150	(*252*)
$Rh_2(CH_3CO_2)_2(acac)_2$	1570, 1560	1440	120, 130	(*237*)
$[Rh(CO)_2(CH_3CO_2)]$	1560	1439	121	(*253*)
$Ru_2Cl(HCO_2)_4$	1480	1336	144	(*160*)
$[Cr_3(H_2O)_3O(CH_3CO_2)_6]Cl$	1595	1515	80	(*254*)
$[Fe_3(H_2O)_3O(CH_3CO_2)_6]Cl$	1595	1450	145	(*167*)
$Pd_3(CH_3CO_2)_6$	1600	1427	173	(*252*)
$Be_4O(CH_3CO_2)_6$	1640	1487	153	(*255*)
$Fe_4O(CH_3CO_2)_{10}$	1627, 1560	1454, 1380	106–247	(*169*)

[a] Abbreviations: pdp = 1-phenyl-2,3-dimethyl-5-pyrazolone; fur = furan 2-carboxylate.

Using the criterion that the antisymmetric CO_2-stretching frequency of a binuclear copper(II) carboxylate is higher than that for the corresponding sodium salt, the observation of a lower frequency for $Cu(CF_3CO_2)_2$ (1650 cm^{-1}) than for $NaCF_3CO_2$ (1680 cm^{-1}) was considered to support the conclusion reached by magnetic studies that the compound was not dimeric (*256*). A study of copper(II) salts of α,ω-dicarboxylic acids showed that the spectrum of copper(II) malonate was almost identical with that of sodium malonate (*257*), whereas for the other copper compounds the antisymmetric stretches were higher in frequency than for the corresponding sodium salt, in line with the notion that only the malonate is not antiferromagnetic (*100*).

The most revealing study of copper(II) carboxylates was that of Heyns (*258*) who studied the temperature dependence of infrared spectra between 350 and 77 K. He concluded that splittings of about 30 cm^{-1} in one of the CO_2-stretching modes might be caused by coupling of vibrations of a number of carboxylate groups. Discontinuities in plots of peak intensity against temperature were attributed to phase changes in anhydrous and hydrated $Cu_2(CH_3CO_2)_4$, but it is curious that no comparable anomalies have been seen in the magnetic data for these well-studied compounds.

Molybdenum(II) carboxylates also show a splitting of 8–12 cm^{-1} in the antisymmetric stretching mode, which possibly is caused by the coupling of carboxylate groups mentioned above but which was originally attributed (*155*) to different configurations of the carboxylate ligands. Subsequent X-ray analysis (*28*) showed the acetate to contain only bridging groups. Also, the small separation of 103 cm^{-1} between the CO_2-stretching frequencies invalidates the assumption that a separation of less than the free ion value indicates a chelating configuration.

In $V_2(CH_3CO_2)_6$ and $V_2(C_6H_5CO_2)_6$, the antisymmetric stretching mode was split into two components separated by about 40 cm^{-1}. This splitting is retained in solution and suggests that the compounds have the usual $M_2L_2(RCO_2)_4$ structure with monodentate carboxylate groups acting as terminal ligands (*146*).

Compounds $Rh_2(CH_3CO_2)_2(\text{diket})_2$, where diket is the anion of a β-diketone, and their adducts with 2 molecules of water or pyridine have infrared spectra that indicate bridging acetate groups (*237*). The rhodium(I) complex $[Rh(CO)_2(CH_3CO_2)]$ probably also has a structure of 2 rhodium atoms bridged by 2 acetate groups with the four remaining in-plane sites occupied by carbon monoxide molecules (*253*).

Dimeric complexes $Pd_2L_2(RCO_2)_4$, where L is Ph_3P, Ph_3As, or Me_2CO and R is CH_3, CF_3, or C_2F_5, have two bands for each CO_2-stretching mode. This was thought to represent cis and trans isomers of a structure with square-planar palladium atoms and monodentate and bridging carboxylate groups (*259*), but the splittings could also be due to coupling of vibrations in the usual dimeric structure.

The difficulty of assigning bands in these spectra is illustrated by $[Fe_3(H_2O)_3O(CH_3CO_2)_6]Cl$, for which the symmetric CO_2 stretch has been variously located at 1450 cm^{-1} (*167*) or at the abnormally low position of 1335 cm^{-1} (*254*). The observation of an apparently high frequency of 1699 cm^{-1} for the antisymmetric CO_2 stretch in the compound formulated (*172*) as $H^+[V_3O(CH_3CO_2)_8]^-$ was better explained (*173*) as being due to coordinated acetic acid in the vanadium analog of "anhydrous manganese(III) acetate," i.e., $[V_3(CH_3CO_2H)(CH_3CO_2)_{2/2}O(CH_3CO_2)_6]_\infty$. In a study (*178*) of a series of trinuclear complexes $[M_3L_3O(CH_3CO_2)_6]^+$, where L is pyridine or 3-picoline, the CO_2-stretching frequencies showed shoulders in the cobalt(III) complexes, but these were not seen in the complexes of other metals. It was concluded that the structure of the cobalt complexes differed (Fig. 31) from the other metal complexes. The shoulders could be caused by coupling of acetate groups; nevertheless, the conclusion is supported by NMR spectra and X-ray powder diffraction data. Unusual structures were also proposed (*177*) for some carbon monoxide adducts of ruthenium carboxylates, such as $Ru_3CO(py)_2O(CH_3CO_2)_6$ (Fig. 22) and $Ru_2CO(Ph_3P)O(CH_3CO_2)_3$, but for these only the antisymmetric stretch was located; further crystallographic confirmation is needed.

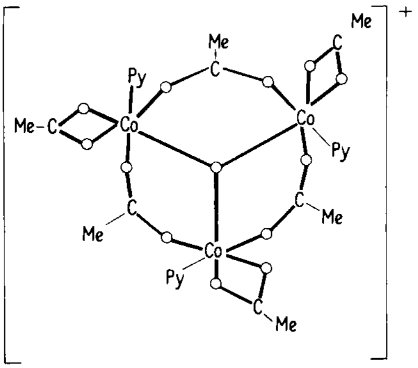


FIG. 31. Proposed structure of the $[Co_3(py)_3O(CH_3CO_2)_6]^+$ cation. [From Wilkinson *et al.* (*178*), by permission.]

There are so few cluster carboxylates with more than 3 metal atoms in each molecule that one cannot deduce correlations between structure and vibrational spectra for them. Splittings of up to 84 cm^{-1} in the CO_2-stretching modes of $Fe_4O(CH_3CO_2)_{10}$ and $[Fe_5O(CH_3CO_2)_{12}]$-(CH_3CO_2) indicate the presence of a variety of coordination modes, and proposed structures for these clusters are given in Figs. 32 and 33, but again crystallographic work is required (*180*). In complexes $Cu_2(diene)(CH_3CO_2)_2$, separations of 147 to 164 cm^{-1} were found (*260*) appropriate for the retention of the $Cu_2(CH_3CO_2)_2$ unit of the polymeric uncomplexed acetate (Fig. 16), but a complete structure was not proposed. In numerous other copper(I) carboxylates, the distinct differences in the separations of the CO_2-stretching modes from those found in $Cu(Ph_3P)_3(RCO_2)$, in which the carboxylates are almost certainly monodentate, indicate (*261*) that they also have the polymeric structure.

All the examples so far discussed have used analysis of the CO_2-stretching modes to predict molecular structures, but it would be

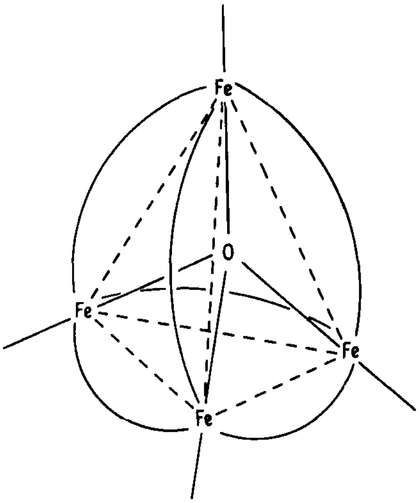


FIG. 32

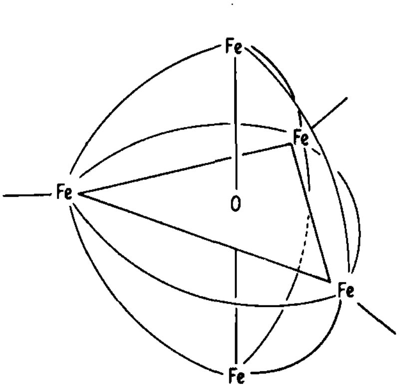


FIG. 33

FIG. 32. Proposed structure of $Fe_4O(CH_3CO_2)_{10}$. Fe⌒Fe, bridging acetate; Fe—, terminal acetate.

FIG. 33. Proposed structure of the $[Fe_5O(CH_3CO_2)_{12}]^+$ cation. Fe⌒Fe, bridging acetate; Fe—, terminal acetate.

more useful if the vibrations of the metal–oxygen units could be identified. These lie below the range of older infrared spectrophotometers, but there have been a few assignments in the 200–650 cm^{-1} region, often without the necessary theoretical treatment or experimental confirmation. Examples of these speculative assignments are those of copper(II) acetate and the various chloroacetates (*262*) and of many beryllium carboxylates (*255*, *263*). It is particularly unfortunate that this work is not more rigorous and is unsupported by crystallography, as many tantalizing formulas are involved, such as $Be_6O_2(CH_3CO_2)_8$ and $Be_4O(CH_3CO_2)_5(C_2H_5O)$, with attractive structures proposed from the "Be—O" vibrations. Isotopic substitution with ^{65}Cu has allowed assignment (*264*) of copper–oxygen and copper–nitrogen frequencies. In dimeric carboxylates, the Cu—O stretching vibrations lie between 300 and 400 cm^{-1}. Vibrations above 400 cm^{-1} are not shifted on isotopic substitution and are probably internal modes of the ligands. The shift in Cu—O frequencies on substitution with ^{65}Cu is about 5 cm^{-1}, but some bands shift by only 2 cm^{-1} or less, and these are believed to be mixed modes including both Cu—O and ligand contributions. Some amine adducts, in either the classes of dimeric complexes with pyridines or polymeric complexes with anilines, show an isotopically sensitive band near 240 cm^{-1}, probably the Cu—N stretching vibration. The Rh—O stretching vibrations in $[Rh_3(H_2O)_3O(CH_3CO_2)_6]ClO_4 \cdot 2H_2O$ are said (*265*) to occur at 302, 382, and 397 cm^{-1}, but shifts of the first and last of these bands by 4 and 17 cm^{-1}, respectively, in the trideuteroacetate give doubts on the assignment.

The very short metal–metal separations in binuclear carboxylates of the 4*d* and 5*d* transition elements have prompted searches for M—M stretching modes in the Raman spectra. These vibrations have been claimed as the remarkably intense bands that are found in similar positions in a range of molybdenum(II) or rhenium(III) compounds, including halides and sulfato complexes as well as carboxylates. For $Mo_2(RCO_2)_4$ species, the Mo—Mo stretching mode occurs between 396 and 406 cm^{-1} (*29*, *266–269*). The force constants indicate a bond order of 3 to 4, agreeing with the assignment of a quadruple Mo—Mo bond in these compounds. One of the reports (*268*) draws attention to the higher Mo—Mo frequency in carboxylates than in $K_4Mo_2Cl_8$, which has this band at 350 cm^{-1} although having a very similar Mo—Mo bond length to the carboxylates. In fact, addition of axial ligands to $Mo_2(RCO_2)_4$ lowers the frequency of this band as far as 367 cm^{-1}, with stronger ligands giving a greater shift (*267*, *268*) even though there is only a 2% lengthening in the Mo—Mo bond in $Mo_2(py)_2(CF_3CO_2)_4$ over $Mo_2(CF_3CO_2)_4$ (*30*). The Re—Re stretching mode has been located at 284–289 cm^{-1} in $Re_2(CH_3CO_2)_4X_2$, at 277–279 cm^{-1} in $Re_2(CH_3CO_2)X_4 \cdot 2H_2O$(X = Cl, Br), and at 216 cm^{-1} in $Re_2OCl_5(CH_3CO_2)(PPh_3)_2$ and $Re_2OCl_3(CH_3CO_2)_2(PPh_3)_2$ (*269*). The Rh—Rh stretching mode in $Rh_2(RCO_2)_4$ has been identified (*268*) at about 350 cm^{-1}, again being decreased on complex formation with 2 ligand molecules. Other workers (*269*) did not make a definite assignment but conjectured that this vibration may occur at 170 cm^{-1}. They were also unable to identify a Cu—Cu vibration in $Cu_2(H_2O)_2(CH_3CO_2)_4$.

VII. Nuclear Magnetic Resonance Spectroscopy

The proton magnetic resonance spectra of metal complexes often yield information concerning the molecular structure and magnetic susceptibility of a complex and the delocalization of unpaired electron-spin density from a paramagnetic transition metal to the ligands (*270*). In many paramagnetic compounds the electron-spin relaxation times are too long to give sharp NMR lines, but in polynuclear carboxylates the spin exchange provides an additional mechanism for relaxation time and the spectra can occasionally be resolved.

The ^1H NMR spectrum of a single crystal of $Cu_2(H_2O)_2(CH_3CO_2)_4$ has been reported (*271*). A discussion of the temperature dependence of the line shape and the spin-lattice relaxation time over the range 77–300 K was based on a theory for a fluctuating local magnetic field due to the triplet species. The ^{63}Cu spectrum of a crystal of this compound showed (*272*) splitting due to the quadrupole of the copper nucleus ($I = \frac{3}{2}$). A 5% change in this splitting was interpreted as indicating a δ bond rather than a σ bond between the copper atoms. A value of $310\ \text{cm}^{-1}$ was found for the singlet–triplet separation in $Cu_2(H_2O)_2(CH_3CO_2)_4$ by studying the proton spin-lattice relaxation time (T_1) and using the formula (*273*)

$$\frac{1}{T_1} \propto \frac{3\exp(-\Delta/kT)}{1 + 3\exp(-\Delta/kT)} \tag{19}$$

The proton NMR spectra of several copper(II) arylcarboxylates in $(CD_3)_2CO$ and the urea adducts of copper(II) formate and acetate in $(CD_3)_2SO$ all exhibited contact shifts (*274*). The isotropic shifts were taken as the difference between the chemical shifts of the copper(II) complex and those of a similar diamagnetic zinc compound, although the structures of the zinc compounds are unknown. The magnitude and direction of the contact shifts indicated that spin density from the Cu^{2+} ions is delocalized into the ligands, supporting at least the notion of a partial contribution from superexchange to the magnetic exchange. Similar contact shifts were seen in the ^1H NMR spectra of two modifications of $Cu(HCO_2)_2$, where the large Cu—Cu separations rule out direct exchange (*275*).

The proton NMR spectrum of $V_2(CH_3CO_2)_6$ in CH_2Cl_2 showed the presence of two kinds of acetate group in the ratio 2:1, consistent with the usual dimeric structure with monodentate acetate groups occupying the axial positions (*146*).

Proton NMR spectra in solution have also been used to show that many carboxylates of 4*d*- and 5*d*-transition metals are diamagnetic and, therefore, have polynuclear structures. Some work of this type has been performed for rhenium (*158*) and ruthenium (*177*) compounds, but there is particular variety in rhodium(II) complexes, with polynuclear carboxylates providing many examples of this comparatively unfamiliar oxidation state (*237, 276, 277*). Besides numerous species with the general formula $Rh_2L_2(RCO_2)_4$ (*252, 276*), compounds $Rh_2L_2(RCO_2)_2(\text{diket})_2$ are believed to have dimeric structures with 2 bridging carboxylate groups, with each rhodium atom coordinated by a chelating diketonate group and the monodentate ligand L (Fig. 34)

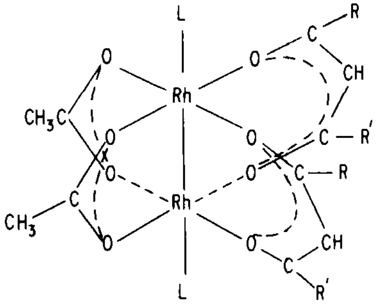


FIG. 34

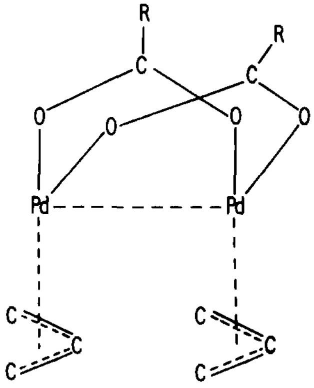


FIG. 35

FIG. 34. Proposed structure of $Rh_2L_2(CH_3CO_2)_2(diket)_2$. [After Ugo and co-workers (*237*), by permission.]

FIG. 35. Proposed structure of $Pd_2(allyl)_2(RCO_2)_2$. [After Robinson and Shaw (*279*), by permission.]

(*237*). The diamagnetic compound $Rh_2(NH_3)_2(H_2O)_2(CH_3CO_2)_4$ has inequivalent acetate groups (*277*), and it was suggested that it contains monodentate and bridging anions. This research group also suggests a dimeric structure for the rhodium(III) compound $Rh_2(NH_3)_2(H_2O)_2(CH_3CO_2)_4(OH)_2$ (*278*).

Many π-allylic palladium(II) complexes with carboxylate bridges were assigned structures from their NMR spectra (Fig. 35) (*279*). A study (*280*) of compounds of the type $Be_4O(CH_3CO_2)_n(CCl_3CO_2)_{(6-n)}$ shows that scrambling of the carboxylate groups occurs in solution.

VIII. Mass Spectrometry

Mass spectrometry is the most misleading techniuqe available to the inorganic chemist seeking to characterize a noncrystalline carboxylate. "Parent ions" appear in the spectrum indicating clusters bigger or smaller than those in the parent molecule, but only occasionally of the right size. The discrepancies may be caused by the necessity to use direct insertion methods for involatile samples and, perhaps, by using an excessively high ionizing energy. (Workers in this field should check for sample pyrolysis and rearrangement reactions.)

For the copper(II) species $Cu_2(H_2O)_2(RCO_2)_4$, where R is CH_3, C_2H_5, C_3H_7, and C_4H_9, ions were found for the dehydrated parent $[Cu_2(RCO_2)_4]^+$ and then down to Cu_2^+ in steps of the successive loss of carboxylate groups (*281*). The spectra were taken at 120°–240°, but this is near the decomposition temperatures of the compounds (*282*). In other studies, including halogenated and arylcarboxylates, no clusters higher than $[Cu_2(RCO_2)_2]^+$ were detected (*283–285*). For the alkylcarboxylates, the principal lines in the spectrum were those of even electron fragment ions formed by the loss of $RCO_2\cdot$ from $[Cu_2(RCO_2)_2]^+$, but, for arylcarboxylates, there were also strong lines for loss of CO_2 with migration of the aryl group to the metal ion, so that from copper(II) benzoate peaks such as $[Cu_2(C_6H_5CO_2)C_6H_5]^+$ were seen. Metastable ions and deuterium substitution were used to identify the lines, which were all considered to be spectra of copper(I) carboxylates believed to be formed by decomposition of the inserted copper(II) carboxylates, since, as the temperature of the probe was gradually raised, peaks for CO_2^+, H_2O^+, RCO_2H^+, and occasionally $(RCO)_2O^+$ and $Cu_4Cl_4^+$ were seen before ions from copper carboxylate species (*285*).

These conclusions were supported by studies (*260, 261, 286, 287*) of spectra from samples of copper(I) carboxylates, which give similar spectra to those seen in the decomposition of copper(II) carboxylates. Most of the copper-containing fragments include 2 metal atoms, with $Cu_2(RCO_2)^+$ forming the strongest peak in most of the spectra. The abundance of dicopper species and the high volatility of the compounds led to the conclusion (*287*) that $Cu_2(RCO_2)_2$ units might be found in the molecular structures, and this has been confirmed for the polymeric acetate (*74, 75*). In some copper(I) carboxylates (*261*), weak lines for larger fragments were detected, e.g. $[Cu_6(CH_2ClCO_2)Cl_4]^+$, $[Cu_3(C_3H_7CO_2)_5]^+$, $[Cu_4(C_6H_5CH{:}CH)C_6H_5]^+$. Metastable ions confirmed that loss of CO_2 or R from $[Cu_2(RCO_2)_2]^+$ was common, but loss of C_2H_4 was also confirmed in $[Cu_2(C_3H_7CO_2)_2]^+$ forming $[Cu_2(C_3H_7CO_2)(CH_3CO_2)]^+$. The formation of chlorine radicals probably explains the formation of polychloro species in the spectrum of copper(I) chloroacetate (*261, 287*).

Parent ions were the only ones found in the mass spectra of $Cr_2(CH_3CO_2)_4$, $Mo_2(CH_3CO_2)_4$, and $Mo_2(C_6H_5CO_2)_4$ at the low ionizing energy of 15 eV (*284*), but $[W(CH_3CO_2)_2]$ gave no tungsten-containing ions and was deduced to be polymeric (*190, 284*). The intriguing compound $CrMo(CH_3CO_2)_4$, formed by the reaction of $Mo(CO)_6$ with $Cr_2(H_2O)_2(CH_3CO_2)_4$, shows a parent ion for the novel heterodinuclear carboxylate and fragments therefrom (*288*). The spectrum also shows peaks from $[Mo_2(CH_3CO_2)_4]^+$, but these can be reduced by using 10 eV as the ionizing energy and must represent products of rearrangement reactions. In a study (*289*) of a range of compounds $Mo_2(RCO_2)_4$, where R was mostly a bulky aryl group, the parent ions were again intense and the principal fragmentations were the loss of $CH_3CO_2\cdot$, $CH_3CO\cdot$, and $CH_2{:}C{:}O$, but successive or simultaneous loss of the same fragment was not detected. For $Mo_2(HCO_2)_4$ loss of CO_2 was an important process, presumably leaving an ion with an Mo—H bond. In all these spectra the Mo—Mo bond was retained, indicating its great strength. The very volatile $Mo_2(CF_3CO_2)_4$ resembles the formate in releasing CF_2CO_2 fragments and forming Mo—F species, such as $[Mo_2F_3(CF_3CO_2)]^+$ (*29*), although here the same fragmentation was repeated. In none of these reports was the ion $Mo_2{}^+$ claimed. It was suggested (*281*) that the fragmentations were controlled by the fragment ions tending to show effective oxidation states of II or III.

Trifluoroacetates seem to be specially volatile and suitable for mass spectral studies. The only rhodium(II) carboxylate to give rhodium-containing species in its mass spectrum (*290*) was $Rh_2(CF_3CO_2)_4$. Besides the parent ion, lines were found for $[Rh_2(CF_3CO_2)_{1-3}]^+$, Rh_2OF^+, Rh_2F^+, Rh_2O^+, and $Rh_2{}^+$, the last of these being the only recorded example of an $M_2{}^+$ ion in a carboxylate's mass spectrum. It is possible that $Tl(CF_3CO_2)_3$ is dimeric since its mass spectrum included lines due to $[Tl_2(CF_3CO_2)_3]^+$ and $[Tl_2(CF_3CO_2)]^+$ but, as for rhodium, these peaks were not found for the acetate or benzoate (*291*).

The mass spectra of the complexes $M_2L_2(CO)_4(CH_3CO_2)_2$ (M = Ru, L = Ph_3P; M = Os, L = Ph_3P, Ph_3As) supported the dimeric formulation (*292*); although parent ions were not seen, $[M_2L(CO)_4(CH_3CO_2)_2]^+$ was prominent.

Among the larger clusters, mass spectra have been used to characterize mixed carboxylates $Be_4O(CH_3CO_2)_n(CCl_3CO_2)_{6-n}$, for which $[Be_4O(RCO_2)_5]^+$ was the base peak (*280*). A similar result was found in the mixed zinc carboxylates with the same structure (*293*), but a curious feature of these spectra is the occurrence of metastable ions at m/e values greater than the parent ions. These were attributed to the reaction

$$[Zn_4O(RCO_2)_6]^{2+} \longrightarrow [Zn_4O_2(RCO_2)_3]^+ + [RCO]^+$$

For cobalt(II) and zinc(II) tetranuclear carboxylates, the parent ions were all detected (*294*), but they were much stronger for cobalt than for zinc. This finding was explained by internal electron transfer to give even electron species such as $[Co_3(II)Co(III)O(RCO_2)_6]^+$, which is unlikely for zinc. The researchers used metastable ions to identify many fragmentations, with the neutral species released including $M(RCO_2)_2$ and $CoO(RCO_2)$, the latter being an uncharacterized cobalt(III) carboxylate. Many trinuclear ions were detected, apparently derived from $[M_3O(RCO_2)_3]^+$, which is a prominent peak in the spectrum.

The base peak for the mass spectrum of crystalline $[Fe_3(CH_3OH)_3O(Me_3CCO_2)_6]^+Cl^-$ is, very misleadingly, $[Fe_4O(Me_3CCO_2)_6]^+$, and there are numerous other heavy ions present such as $[Fe_5O_3(MeCCO_2)_6]^+$ and $[Fe_6O_3Cl(Me_3CCO_2)_{10}]^+$ which must result from complex recombinations in the spectrometer (*295*). With this result in mind, one must be cautious in interpreting the mass spectrum of the noncrystalline 1:1 electrolyte $[Fe_5O(CH_3CO_2)_{12}]^+(CH_3CO_2)^-$, whose cation's proposed structure is shown in Fig. 33 (*180*). The base peak is $[Fe(CH_3CO_2)_2]^+$ and among the polynuclear ions identified are $[Fe_3O(CH_3CO_2)_4]^+$, $[Fe_4O(CH_3CO_2)_7]^+$, and $[Fe_5O(CH_3CO_2)_9]^+$. The last of these may originate from the release of the monodentate CH_3CO_2 groups from the parent cation. As in many of the examples in this section, peaks and transitions were assigned by observation of appropriate metastable ions, the correct distribution of polyisotopic peaks, and accurate mass determination.

IX. Mössbauer Spectroscopy

Although the Mössbauer effect has been observed in many nuclei, only the carboxylates of iron have been studied with this technique. Spectra have been obtained for several basic iron(III) carboxylates containing the structural unit $[M_3L_3O(RCO_2)_6]^+$ (*166*, *167*, *296–298*). They show two broad bands of different intensity. The isomer shifts (0.2–0.8 mm sec^{-1}) and quadrupole splittings (0.45–0.72 mm sec^{-1}) relative to metallic iron are typical of high-spin iron(III) compounds, and there was the expected slight increase in isomer shift at lower temperatures. The higher values of the quadrupole splitting occur for trichloroacetate and phenylacetate complexes; possibly the electron-withdrawing CCl_3 and $C_6H_5CH_2$ groups are responsible for the larger electric field gradient at the nucleus. The quadrupole split lines are rather broad, and from the broadening (*167*) and other experiments (*296*) it has been suggested that the iron atoms are in slightly inequivalent sites, as is also indicated by magnetic susceptibility studies. However, as discussed in Section III,C, it is extremely hard to prepare samples of these compounds free from impurities, and some abnormal results may arise from contamination. Curiously, $[Fe_3(H_2O)_2O(CH_3CO_2)_6]^+CH_3CO_2^-$ is said to have 3 equivalent iron atoms, although only 2 of them can be coordinated by water (*297*).

The quadrupole split lines are of unequal intensity, and this asymmetry increases with increasing temperature. This has been attributed

(*167*) to anisotropy in the recoil-free fraction—the Gol'danskii–Karyagin effect—but another possibility is intermolecular spin–spin relaxation affecting the magnetic hyperfine interactions(*298*). For $[Fe_3(H_2O)_3O(CH_3CO_2)_6]Cl{\cdot}5H_2O$, the asymmetry change was most rapid between 66 and 68 K, suggesting, a hitherto undetected phase change. The possible role of intermolecular interactions suggests that useful experiments may be carried out in diamagnetic host lattices.

In the mixed oxidation state compounds $[Fe_3(H_2O)_3O(CH_3CO_2)_6]{\cdot}2H_2O$ and $[Fe_3(py)_3O(CH_3CO_2)_6]_2{\cdot}py$ spectra for high iron(II) and iron(III) were seen together. The temperature dependence of the quadrupole splitting and the isomer shift indicated that intramolecular electron transfer occurred within 10^{-7} sec (*299*).

X. Heat Capacity Measurements

At low temperatures the energy levels that contribute to the heat capacity of a cluster compound are the lattice vibrational levels and those arising from the spin exchange. The spin-exchange component (C_m) may be obtained from

$$C_m = dU/dT \tag{20}$$

where U is the internal energy given by

$$U = NkT^2 \left[d \ln \sum_{S'} (2S' + 1)\omega(S') \exp[-E(S')/kT] \Big/ dT \right] \tag{21}$$

The heat capacity equations for different spin systems and plots of the reduced heat capacity (C_m/Nk) against reduced temperature ($kT/|J|$) are given by Ginsberg (*88*).

Thus heat capacity measurements can be used to study the spin-exchange process provided allowance can be made for the lattice vibrations. Below about 10 K, the lattice heat capacity is very small and the measured heat capacity is almost entirely due to C_m, but at higher temperatures it is necessary to calculate the lattice contribution.

The only carboxylate cluster to have been studied by this technique is $[Cr_3(H_2O)_3O(CH_3CO_2)_6]^+Cl^-{\cdot}6H_2O$. The first measurements (*300*) indicated that the chromium atoms formed on isosceles triangle rather than an equilateral triangle, but later measurements (*301*) indicated that there were two equiabundant sets of isosceles triangles, a result later confirmed by electronic spectral studies (*241*). Phase transitions were found at 211.4 and 215.5 K; these were believed to involve reordering of the water of crystallization.

There is no doubt this technique should be more fully exploited in this field. It may be specially useful in studying compounds in which there are many closely spaced energy levels, so that their population varies appreciably in the helium range of temperatures.

XI. Molecular Weight Determinations

Although the determination of its molecular weight would appear to have a major role in determining the degree of polymerization of a cluster carboxylate, these determinations have not actually been very fruitful. This is because the cluster complexes are usually insoluble in organic solvents, and such solutions as can be made are often excessively dilute or give misleading results due to various decompositions and equilibria. Ebullioscopic methods are more misleading than cryoscopic ones, as the higher temperature seems to give more decomposition.

The molecular weights of the copper(II) alkylcarboxylates from acetate to valerate (*302*) and several arylcarboxylates (*111*) were found to be close to the dimeric values in dioxane, which is a useful solvent in this area despite being hygroscopic. Two dioxane molecules probably coordinate to the metal atoms in the axial positions of the dimer, so that the uncomplexed carboxylates may not be dimeric in the solid state. In water the molecular weights of the copper(II) alkylcarboxylates from acetate to butyrate were less than the monomeric values (*302*), suggesting that the bridged dimer is broken down in the strongly ionizing and coordinating solvent.

The dimeric nature of various compounds of the types $Rh_2(C_2H_5OH)_2(RCO_2)_4$ (*276*) and $Rh_2L_2(RCO_2)_2(\mathrm{diket})_2$ (*237*) have been established by cryoscopy and vapor pressure techniques, respectively, in benzene, but the values are often a little low. Palladium(II) acetate and propionate are trimeric in benzene at 37°C, but ebullioscopic measurements showed they were monomeric in boiling benzene (*252*). However the benzoate was trimeric in boiling benzene and chlorobenzene.

XII. Conclusions

The interpretation of the physical properties of carboxylate clusters often requires very subtle developments in the theory of the technique being used. This means that these unusual compounds not only provide interesting problems for synthetic inorganic chemists and for crystallographers but also offer a challenge throughout the field of chemical physics. However, there is no doubt that the most striking advances are made when a variety of techniques is applied to the same compound, as in the magnetochemistry, electronic spectra, and heat capacity studies of trinuclear chromium(III) carboxylates, and in the complementary use of magnetochemical and EPR measurements in initiating studies on $Cu_2(H_2O)_2(CH_3CO_2)_4$ and so opening the whole field. Finally, we emphasize the major importance of X-ray structural studies. Attempted structural assignments from noncrystallographic methods have often proved hazardous, and the role of these techniques should always be to elucidate bonding patterns or following reactions once the basic molecular structure has been established by diffraction methods.

XIII. Appendix

This section includes some recent results that became available after earlier sections were written.

The copper–copper separation in $Cu_2(urea)_2(CH_2ClCO_2)_4$ is 2.651 Å (*303*). Copper(II) octanoate and decanoate have polymeric structures based on $Cu_2(RCO_2)_4$ units, with Cu—Cu separations of 2.63 and 2.59 Å and axial Cu—O distances of 2.24 and 1.91 Å (*304*). The pyrazine complex $Cu(pyr)(CH_3CO_2)_2$ has been shown crystallographically to have the polymeric structure (Fig. 26) implied by EPR spectra, which the paper also discusses (*305*). The singlet–triplet separation in $Cu_2(quin)_2(CF_3CO_2)_4$ is 310 cm^{-1} (*13*). A Russian review covers crystal and EPR data of copper carboxylates (*306*).

The structure of $Mo_2(CH_3CO_2)_4$ has been redetermined (*307*). The Mo—Mo separation is 2.094 Å and the axial oxygens are 2.645 Å from the molybdenum atoms. Various complexes of the type $[Mo_2(CF_3CO_2)_4X_n]^{n-}$ have been prepared (*308*). The Raman spectra show ν Mo—Mo at 382–366 cm^{-1}. The anion $[Mo_2(CF_3CO_2)_3Cl_3]^{2-}$ has also been prepared in this work and may represent a new type of structure. Two binuclear palladium(II) acetates are known, both having two bridging acetate groups but not Pd—Pd bonds (*309*, *310*).

The cation of $[Fe_3(MeOH)_3O(Me_3CCO_2)_6]Cl$ has the usual triangular configuration (*295*). The central oxygen atom is 0.24 Å above the Fe_3 plane. Cobalt shows an effective oxidation state of $2\frac{2}{3}$ in $Co_3L_3O(RCO_2)_6$, whose room temperature magnetic moments range from 2.11 to 4.38 μ_B, and whose electronic spectra are those of octahedral cobalt(III) complexes (*311*). Two ruthenium(III) complexes of the type $[Ru_3L_3O(CH_3CO_2)_6]$ ($L_3 = 3CH_3OH$ or $2H_2O + OH^-$) have been reported (*312*); they have magnetic moments of 2.16 and 2.04 μ_B, respectively, at 293 K.

Niobium(IV) ·forms a trinuclear formate $[(C_5H_5)_3Nb_3O_2(OH)_2(HCO_2)_3]$ (*313*). The structure consists of a $(C_5H_5)_3Nb_3O(HCO_2)_3$ triangle, with a cyclopentadienyl group bonded to each metal atom, the oxygen atom bridging all 3 niobium atoms and a formate group bridging each pair of niobium atoms. Two pairs of niobium atoms are also bridged by an hydroxyl group (Nb—Nb = 3.136 Å) and one pair is bridged by the second oxygen atom (Nb—Nb = 3.149 Å). The magnetic moment of the complex is 1.17 μ_B at 295 K and 1.00 μ_B at 77 K. These data are said to indicate a J value of -156 cm^{-1}, but contributions from spin-orbit coupling and second-order Zeeman effects were not included.

Reviews have been published on complexes containing the $CF_3CO_2^-$ ion (*314*) and on dimers with monatomic bridges (*315*). Although the latter does not deal with carboxylates, the importance of the M—O—M bridging angle in determining the sign and magnitude of the exchange in simple dimers indicates a possible line of study for carboxylates and related compounds.

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