Magnetic and Spectroscopic Study of some Binuclear and Trinuclear Cobalt(II) Carboxylate Complexes†

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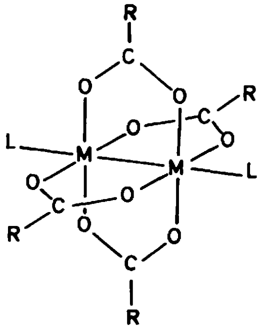
Binuclear $[Co_2(RCO_2)_4L_2]$ and trinuclear $[Co_3(RCO_2)_6L_2]$ cobalt(II) carboxylate complexes have been prepared (R = unsaturated alkyl, L = sterically hindered amine). The roles of electronic and steric effects on the formation of oligonuclear cobalt(II) carboxylates are discussed. The temperature dependence of their antiferromagnetism shows variations as R and L are altered.

Since van Niekerk and Schoening[1] first demonstrated the binuclear nature of $Cu(MeCO_2)_2{\cdot}H_2O$ there has been considerable interest in binuclear carboxylate-bridged complexes $M_2(RCO_2)_4L_2$ (M = Mo^{II}, Cr^{II}, W^{II}, Rh^{II}, Re^{III}, or Cu^{II}). The carboxylate bridges provide a framework within which a wide variety of metal–metal interactions may occur, ranging from the formally quadruple bond in complexes with the ${Mo^{II}}_2{}^{4+}$ core[2] to the weak metal interactions in ${Cu^{II}}_2{}^{4+}$ species.[3]



Our interest lies in oligonuclear complexes containing weak or non-existent bonding interactions, an area currently dominated by studies of binuclear copper(II) carboxylate systems. We have recently reported the preparation and structure of the binuclear zinc carboxylate complex[4] $[Zn_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$ (C_9H_7N = quinoline) and the linear trinuclear zinc carboxylate complex[5] $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$; there is much in common between the structural chemistry of zinc(II) and cobalt(II) carboxylates[5–8] which prompted us to attempt to prepare some new polynuclear cobalt(II) carboxylates with the aim of making a systematic study of their magnetic, spectroscopic, and structural properties. Relatively few relevant investigations have previously been reported; the crystal structures of $[Co_2(PhCO_2)_4(C_9H_7N)_2]$[8,9] and $[Co_3(PhCO_2)_6(C_9H_7N)_2]$[7] have been reported, as has that of a very closely related binuclear 4-methylquinoline adduct[10] as a prelude to a thorough study of its magnetic properties.[11] The only other work has been that of Pasynskii *et al.*[12] who described the preparations of quinoline and 2-methylpyridine (2Me-py) adducts of cobalt(II) pivalate.

We report here the preparations of a series of binuclear cobalt(II) complexes using α,β-unsaturated carboxylic acids, and a study of their magnetic and spectroscopic properties. In the course of this investigation we have also prepared several new mononuclear and trinuclear complexes.

Results and Discussion

It has been recognised[13] that cobalt(II) is reluctant to form binuclear carboxylate-bridged complexes; there are many examples of rhodium(II) and copper(II) binuclear species but it is the mononuclear complexes of cobalt(II) which abound.[14] The major factor encouraging binuclear complex formation with cobalt is the presence of steric crowding around the metal atoms, caused by the co-ordination of sterically demanding carboxylate groups and 2-substituted heterocyclic amines. This restricts the formation of bis(amine) adducts. The inductive electron-releasing electronic factor mentioned by Pasynskii *et al.*[12] is less important because both benzoic and 2-nitrobenzoic acid, for which binuclear complexes are known,[8] have lower pK_a values (4.19 and 2.17 at 25 °C) than acetic acid (4.75 at 25 °C); the latter has been extensively studied and shows no tendency to form binuclear cobalt(II) carboxylate complexes. Thus, it was decided that α,β-unsaturated aliphatic carboxylates were likely to promote binuclear complex formation; they possess unsaturation in conjugation with the carboxylate moiety, which results in a degree of steric hindrance not present in most saturated aliphatic carboxylates hitherto studied.

Table 1 lists the complexes prepared together with their microanalytical data. As expected, no binuclear complex could be prepared using heterocyclic amines other than those substituted in the 2 position (even when α,β-unsaturated carboxylates were present). Vinylacetic acid, in which the double bond is out of conjugation with the carboxylate moiety, also did not form a binuclear complex. This strongly infers that the factors promoting dimer formation (carboxylate and amine steric hindrance) must be present simultaneously.

The preference for binuclear *vs.* trinuclear complex formation can be influenced by subtle factors such as changes in the amount of amine present, or the reaction temperature.[6] However, work in this laboratory[15] has resulted in the preparation of $[Co_3(PhCO_2)_6L_2]$ (L = isoquinoline); the presence of an amine substituted in the 3 position infers that the steric hindrance due to the amine, and necessary for dimer formation, is not an important factor for trinuclear complex formation.

Diffuse-reflectance visible spectra of the green binuclear complexes consist of three characteristic bands (Table 2). These have been assigned[6] on the basis of a square-pyramidal $NCoO_4$ chromophore with C_{4v} symmetry and the transitions arise from the $^4A_2$ ground state to $^4B_1$, ^4E, and $^4A_2$ excited states

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† *Non-S.I. unit employed:* B.M. ≈ 9.27×10^{-24} A m^2.

Table 1. Analytical data (%)

Compound	Found				Required			
	Co	C	H	N	Co	C	H	N
$[Co(MeCH{=}CHCO_2)_2(4CN\text{-}py)_2]$	—	54.4	4.30	12.55	—	54.95	4.10	12.8
$[Co(CH_2{=}CMeCO_2)_2(4CN\text{-}py)_2]$	13.2	54.9	4.10	12.7	13.5	54.95	4.10	12.8
$[Co_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$	16.1	57.2	4.75	3.85	16.45	57.0	4.80	3.90
$[Co_2(MeCH{=}CHCO_2)_4(2Me\text{-}py)_2]$	18.35	52.0	5.15	4.20	18.3	52.2	5.30	4.35
$[Co_2(CH_2{=}CMeCO_2)_4(C_9H_7N)_2]$	16.05	57.3	4.80	3.90	16.45	57.0	4.80	3.90
$[Co_2(CH_2{=}CMeCO_2)_4(2Me\text{-}py)_2]$	17.95	52.2	5.20	4.25	18.3	52.2	5.30	4.35
$[Co_2(MeCH{=}CMeCO_2)_4(C_9H_7N)_2]$	15.4	59.3	5.45	3.55	15.25	59.05	5.50	3.65
$[Co_2(MeCH{=}CMeCO_2)_4(2Me\text{-}py)_2]$	16.65	54.95	6.00	3.95	16.8	54.85	6.05	4.00
$[Co_2(Me_2C{=}CHCO_2)_4(C_9H_7N)_2]$	15.2	59.1	5.35	3.60	15.25	59.05	5.50	3.65
$[Co_3(CH_2{=}CMeCO_2)_6(2Me\text{-}py)_2]$	20.0	49.4	4.95	3.05	20.25	49.5	5.10	3.20
$[Co_3(Me_2C{=}CHCO_2)_6(2Me\text{-}py)_2]$	18.2	52.65	5.75	2.85	18.45	52.55	5.90	2.95

Table 2. Spectroscopic data

Compound	Vibrational data[a]/cm^{-1}		Diffuse-reflectance data/nm
	$\nu_{sym}(COO)$	$\nu_{asym}(COO)$	
$[Co(MeCH{=}CHCO_2)_2(4CN\text{-}py)_2]$	1 412 (1 435)	1 581 (1 563)	473(sh), 503
$[Co_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$	1 417	1 593	445, 588, 735
$[Co_2(MeCH{=}CHCO_2)_4(2Me\text{-}py)_2]$	1 412	1 597	443, 580, 710
$[Co_2(CH_2{=}CMeCO_2)_4(C_9H_7N)_2]$	1 410 (1 421)	1 594 (1 560)	453, 588, 743
$[Co_2(CH_2{=}CMeCO_2)_4(2Me\text{-}py)_2]$	1 416	1 600	453, 580, 735
$[Co_2(MeCH{=}CMeCO_2)_4(C_9H_7N)_2]$	1 406 (1 412)	1 592 (1 557)	448, 588, 738
$[Co_2(MeCH{=}CMeCO_2)_4(2Me\text{-}py)_2]$	1 409	1 592	452, 578, 715
$[Co_2(Me_2C{=}CHCO_2)_4(C_9H_7N)_2]$	1 410 (1 410)	1 588 (1 560)	450, 586, 743
$[Co_2(Me_3CCO_2)_4(C_9H_7N)_2]$[b]	1 420 (1 415)	1 610 (1 552)	—
$[Co_2(Me_3CCO_2)_4(2Me\text{-}py)_2]$[b]	1 420	1 610	—
$[Co_3(CH_2{=}CMeCO_2)_6(2Me\text{-}py)_2]$	1 407 (1 421)	1 529, 1 589 (1 560)	554
$[Co_3(Me_2C{=}CHCO_2)_6(2Me\text{-}py)_2]$	1 411 (1 410)	1 537, 1 556, 1 620 (1 560)	550

[a] All absorptions are strong; values in parentheses are for the corresponding ionic sodium carboxylate. [b] Initially prepared by Pasynskii *et al.*[12] but no vibrational data supplied.

respectively. The purple trinuclear complexes exhibit spectra consistent with cobalt(II) in a trigonal-bipyramidal environment of D_{3h} symmetry, indicating that the terminal cobalt atoms dominate the spectrum, with slight differences owing to deviations from D_{3h} symmetry.

Comparison of the solid-state and solution spectra reveals that the oligomeric structures are not maintained in solution. The solution (EtOH, MeOH, or $CHCl_3$) spectra are typical of cobalt(II) in an octahedral environment, and are very similar to that of $[Co(H_2O)_6]^{2+}$. However, when $[Co_2(MeCH{=}CHCO_2)_4(C_9H_7N)_2]$ is dissolved in quinoline there is evidence to suggest that it retains its dimeric structure; the visible spectrum consists of two peaks, at 406 and 537 nm ($\varepsilon_{max.}$ = 333 and 268 cm^2 mol^{-1} per dimer unit, respectively), which are similar to those for the transitions to $^4A_2$ and ^4E states observed in the solid-state spectrum. This behaviour agrees with the criteria proposed for dimer *versus* monomer formation, since in a co-ordinating solvent one would expect the solvent to exchange with quinoline, forming a dynamic equilibrium. However, the consequent loss of steric hindrance at the dimer axial positions causes monomer formation. With quinoline as the solvent, the solvent–ligand equilibrium would not result in loss of steric hindrance so the binuclear structure is retained.

For the binuclear complexes, the carboxylate stretching frequencies (Table 2) are consistent with the presence of bidentate *syn-syn* bridging.[16] No significant shift in the $\nu(C{=}C)$ band was observed, compared with the corresponding sodium salts.

The carboxylate stretching region in the i.r. spectra of the linear trinuclear complexes is more complicated than that for the dimers (Table 2). An extra peak occurs on the low-frequency side of the asymmetric stretch and this is characteristic of all linear trinuclear cobalt complexes; it is absent from the spectra of linear trinuclear zinc carboxylates.[4] The crystal structure[7] of $[Co_3(PhCO_2)_6(C_9H_7N)_2]$ shows that two of the carboxylate bridges in the molecule are considerably distorted in such a way that weak monatomic bridges are formed between one of the carboxylate oxygen atoms and two cobalt atoms. It is likely that the extra peak can be assigned to an asymmetric carboxylate stretch, and it is altered in frequency owing to this distortion. The complex $[Co_3(Me_2C{=}CHCO_2)_6(2Me\text{-}py)_2]$ is unique amongst linear trinuclear cobalt complexes as it also exhibits an i.r. absorption at 1 620 cm^{-1}. The spectrum of $[Zn_3(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ shows this absorption,[4] which is assigned as $\nu(C{=}O)$. The effect is caused by a weak $C{=}O\cdots Zn$ interaction which reduces the frequency by approximately 80 cm^{-1} compared with the free carboxylate value. This infers that $[Co_3(Me_2C{=}CHCO_2)_6(2Me\text{-}py)_2]$ possesses a 'true' monatomic bridge, with a weak $C{=}O\cdots Co$ terminal interaction.

Magnetic Measurements.—There has been much work on the magnetic exchange properties of binuclear carboxylate complexes; the majority of it has concentrated on systems in which orbital contributions to the magnetic properties are small, and the exchange process can be considered isotropic. Such systems can be treated using the Van Vleck equation[17] and the relatively simple Heisenberg–Dirac–Van Vleck (hdvv) spin Hamiltonian $H_{hdvv} = -2J_{ij}S_iS_j$ where J_{ij} is the magnitude of the coupling between atoms with spins S_i and S_j; J_{ij} is positive for ferromagnetic interactions and negative for antiferromagnetic

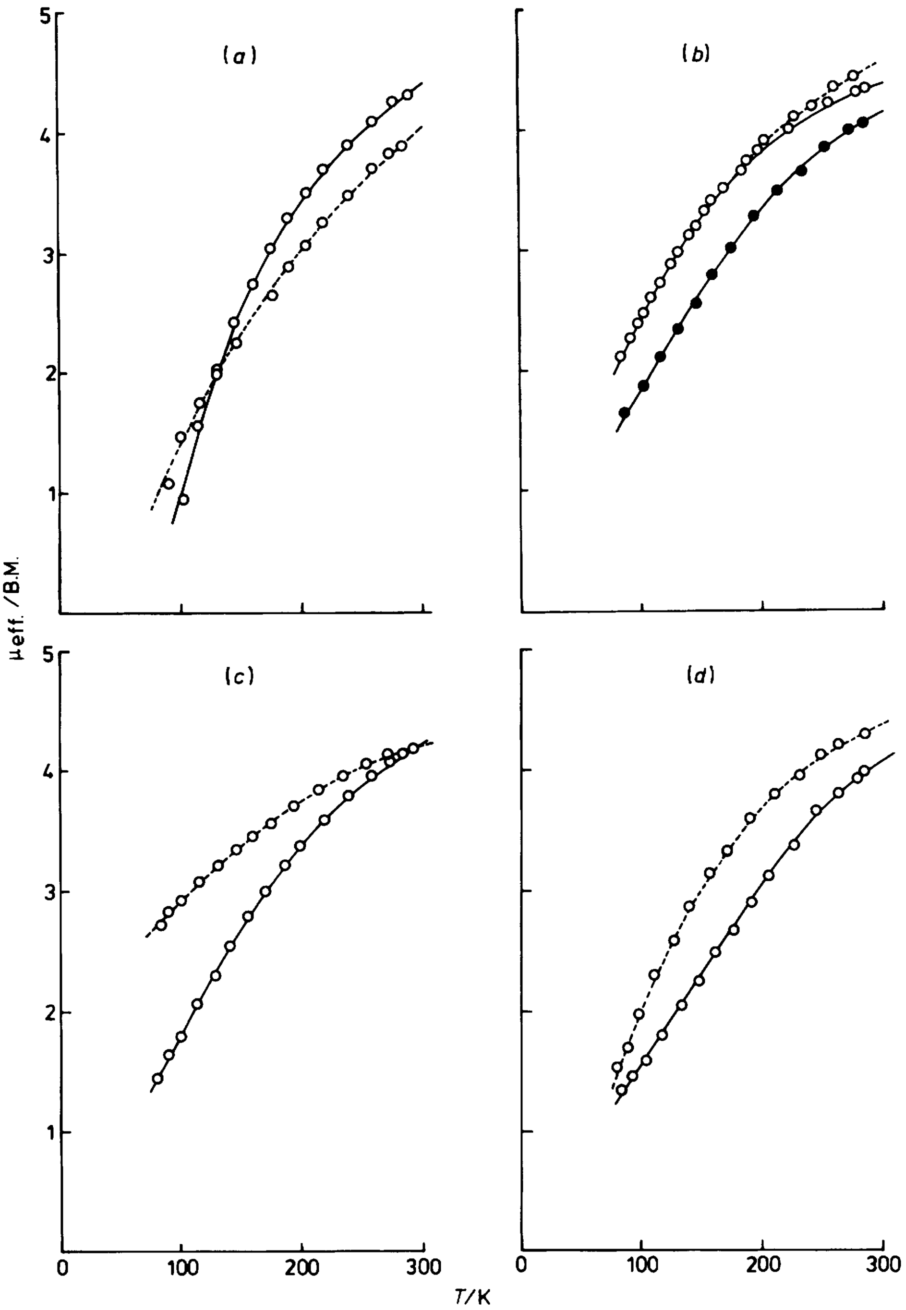

Figure. Variation of effective magnetic moment with temperature over the range 85—285 K for binuclear cobalt(II) carboxylate complexes of quinoline (——) and 2Me-py (---): (*a*) crotonate (*trans*-MeCH=CHCO$_2^-$); (*b*) methacrylate (CH$_2$=CMeCO$_2^-$) and 3,3-dimethylacrylate (Me$_2$C=CHCO$_2^-$) (●); (*c*) 2-methylbutenoate (*trans*-MeCH=CMeCO$_2^-$); and (*d*) pivalate (Me$_3$CCO$_2^-$) complexes

interactions. In particular, the binuclear complexes of copper(II) have been extensively studied in an attempt to determine the exact nature of the coupling process.[18,19]

The theoretical treatment of binuclear cobalt(II) complexes is more difficult than for copper(II) because cobalt(II) has an orbitally degenerate electronic ground state, and orbital contributions have a significant effect on the magnetic exchange process. Boyd *et al.*[11] have made a single-crystal anisotropy study of [Co$_2$(PhCO$_2$)$_4$L$_2$] (L = 4-methylquinoline), interpreting the results within a quantum-mechanical model[20] developed to overcome the limitations of the hdvv approach. Their conclusion was that the antiferromagnetic coupling occurs between metal d_{xy} orbitals, utilising the delocalised π-bonding system of the bridging benzoate groups in a superexchange process.

The binuclear complexes we have prepared also contain carboxylate groups with delocalised π-bonding systems. We decided to carry out a simple powder magnetic susceptibility study to investigate the effect on the magnetic exchange, if any, of subtle changes in the bridging carboxylate framework or the terminal nitrogen-base ligand. Our results show that altering the carboxylate bridge can dramatically affect the coupling. The Figure shows, for example, that $\mu_{eff.}$ for [Co$_2$(MeCH=CHCO$_2$)$_4$(2Me-py)$_2$] varies from 1.14 B.M. at 90 K to 3.92 B.M. at 285 K, and $\mu_{eff.}$ for [Co$_2$(MeCH=CMeCO$_2$)$_4$(2Me-py)$_2$] varies from 2.78 B.M. at 90 K to 4.15 B.M. at 285 K.

Changing the terminal nitrogen-base ligand can also have a significant effect on the exchange process, as illustrated by the cobalt(II) 2-methylbutenoate complexes [Figure (*c*)]. There is a considerable amount of steric crowding present in the axial positions of the binuclear units, so it is likely that altering the nitrogen base causes changes in the co-ordination geometry around each cobalt atom and this changes its magnetic properties.

The magnetic properties of $[Co_3(CH_2{=}CMeCO_2)_6(2Me\text{-}py)_2]$ were investigated, and they proved to be practically identical to those[7] of $[Co_3(PhCO_2)_6(C_9H_7N)_2]$. With a Weiss constant of 19°, $\mu_{eff.}$ for $[Co_3(CH_2{=}CMeCO_2)_6(2Me\text{-}py)_2]$ varies from 4.63 B.M. at 90 K to 4.95 B.M. at 285 K.

This work has demonstrated the use of α,β-unsaturated carboxylic acids and sterically demanding nitrogen heterocycles to promote binuclear cobalt(II) complex formation. It remains uncertain why linear trinuclear complexes should form for certain combinations of carboxylates and nitrogen bases, and apparently not for others; we are currently carrying out a careful investigation into the preparation of oligonuclear cobalt(II) complexes. The subtle variations in the carboxylate bridging mode between different linear cobalt(II) trinuclear complexes is similar in behaviour to that observed[4] in complexes of the type $[Zn_2M(MeCH{=}CHCO_2)_6(C_9H_7N)_2]$ (M^{II} = Zn, Co, Ni, Cd, Mg, Ca, or Sr), where changing M^{II} may significantly alter the bridging mode of the carboxylates. We are currently carrying out *X*-ray crystallographic studies on these complexes in an attempt to rationalise this behaviour.

Experimental

The C, H, and N microanalyses were carried out using a Carlo Erba 1106 elemental analyser. Cobalt analysis was by ethylenediaminetetra-acetate titration.[21] Infrared spectra were recorded from KBr discs (checked by using Nujol and hexachlorobutadiene mulls to ensure no reaction with KBr or compression effects[22]) or from solutions in a 0.2-mm KBr liquid cell on a Perkin-Elmer model 598 spectrometer. Electronic spectra were run on a Perkin-Elmer model 550 spectrometer, using a diffuse-reflectance attachment for samples in the solid state. Magnetic susceptibility measurements were obtained by the Faraday technique using nitrogen as the cryogenic liquid in an assembly outlined in detail elsewhere.[23]

Tetrakis(μ-*crotonato*)-*bis*(*quinoline*)*dicobalt*(II).—The method is based on that described by Catterick and Thornton.[6] Cobalt(II) carbonate, $CoCO_3$ (30 mmol), was refluxed with crotonic acid (66 mmol) in ethanol (100 cm^3) for 6 h. After filtering, quinoline (30 mmol) was added and the mixture refluxed for a further 1 h. The resulting deep purple solution was centrifuged (4 000 revolutions min^{-1} for 20 min) to remove all traces of unreacted carbonate, then concentrated (Rotovap) to a volume of *ca.* 10 cm^3. On standing overnight at 8 °C, green, rhombic crystals formed which were collected by vacuum filtration and washed with a minimum amount of ethanol. The product was dried under vacuum over P_2O_5 at room temperature.

With the exception of tetrakis(μ-methacrylato)-bis(2-methylpyridine)dicobalt(II), all binuclear complexes were prepared by this method. Yields were 20—30% (based on $CoCO_3$).

Bis(4-*cyanopyridine*) *Adducts*.—The dimer procedure was used, resulting in a brown-orange solid. Recrystallisation from ethanol was necessary for purification. Yields were 15—20% (based on $CoCO_3$).

Trinuclear Complexes and Tetrakis(μ-*methacrylato*)-*bis*(2-*methylpyridine*)*dicobalt*(II).—The dimer procedure was employed, using methacrylic acid and 2-methylpyridine, resulting in a purple crystalline trinuclear complex (yield 10%). On addition of excess of 2-methylpyridine to the mother-liquor, the green crystalline dicobalt compound was obtained (yield 15%).

Use of 3,3-dimethylacrylic acid also resulted in a trinuclear complex, but it was not possible to prepare a dimer analogous to the methacrylate compound under similar conditions of excess of base.

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