Rare-earth acetates and formates

$\begin{array}{c c c c c c c c } band & Assignments \\ (range) & Moeller[1] & Patel[3], Nakamoto[4] & Grigor'ev[2] \\ \hline \\ 1545-1565 & \nu_{asy}COO & \nu_{asy}COO & \nu_{asy}COO \\ 1440-1462 & \nu_{sym}COO & \delta_{aso}CH_3 & \nu_{sym}COO \\ 1425-1430 & & \nu_{sym}COO & \nu_{sym}COO \\ \hline \\ 1375-1377 & \nu_{C-C} & \delta_{sym}CH_3 & & \\ p_rCOO & \delta_{sym}CH_3 & & \\ p_rCH_3 & p_rCH_3 & & \\ p_{1010-1020} & p_rCH_3 & p_rCH_3 & & \\ \hline \\ 1050-1057 & & & & \\ 1010-1020 & p_rCH_3 & & p_rCH_3 & & \\ \hline \\ 935-948 & \nu_{CC} & & \nu_{CC} & & \nu_{CC} & & \\ 660-670 & \delta_{COO} & & & & \\ \hline \\ 935-948 & \nu_{CC} & & \nu_{CC} & & \nu_{CC} & & \\ 660-670 & \delta_{COO} & & & & \\ \hline \\ \hline \\ Formate & & & \\ absorption & & \\ band & Assignments & & \\ (range) & Nakamoto[4] & Saralidze et al.[5] & & \\ \hline \\ \hline \\ 1585-1600 & \nu_{asy}COO & & & \\ \hline \\ 1360 & \nu_{sym}COO & & & \\ \hline \\ 1360 & \nu_{sym}COO & & & \\ \hline \\ 1360 & \nu_{sym}COO & & & \\ \hline \\ 780 & \delta_{COO} & & & \\ \hline \\ \end{array}$	Acetate absorption	v. II.	n - Na	1960 S		
$\begin{array}{c c} (range) & Moeller[1] & Patel[3], Nakamoto[4] & Grigor'ev[2] \\ \hline 1545-1565 & \nu_{asy}COO & \nu_{asy}COO & \nu_{asy}COO \\ \hline 1440-1462 & \nu_{sym}COO & \delta_{asy}CH_3 & \nu_{sym}COO \\ \hline 1425-1430 & \nu_{sym}COO & \nu_{sym}COO \\ \hline 1425-1370 & \nu_{C-C} & \delta_{sym}CH_3 & \\ \hline 1050-1057 & \rho_rCH_3 & \rho_rCH_3 & \\ \hline 1010-1020 & \rho_rCH_3 & \rho_rCH_3 & \\ \hline 935-948 & \nu_{CC} & \nu_{CC} & \nu_{CC} & \\ \hline 660-670 & \delta_{COO} & \delta_{COO} & \sigma_{CO} & \\ \hline & & & & \\ \hline 606-620 & & & & \\ \hline Formate \\ absorption \\ band & Assignments \\ (range) & Nakamoto[4] & Saralidze et al.[5] \\ \hline 1585-1600 & \nu_{asy}COO & & \\ \hline 1400-1440 & \rho_rCOO & & \\ \hline 1360 & \nu_{sym}COO & & \nu_{sym}COO \\ \hline 1400-1440 & \rho_rCOO & & \\ \hline 800 & \sigma_{COO} & & \\ \hline 1360 & \nu_{sym}COO & & \\ \hline 1360 & \nu_{$	band		Assignments			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	(range)	Moeller[1]	Patel[3], Nakamoto[4]	Grigor'ev[2]		
$\begin{array}{c ccccc} 1440-1462 & \nu_{sym}COO & \delta_{asy}CH_3 & \nu_{sym}COO \\ 1425-1430 & \nu_{sym}COO & \nu_{sym}COO \\ 1375-1377 & \nu_{C-C} & \delta_{sym}CH_3 \\ 1050-1057 & \rho_rCOO & \delta_{sym}CH_3 \\ 1050-1057 & \rho_rCH_3 & \rho_rCH_3 \\ 935-948 & \nu_{CC} & \nu_{CC} & \nu_{CC} \\ 660-670 & \delta_{COO} & \delta_{COO} & \pi_{COO} \\ & & & & & & & & \\ 660-670 & \delta_{COO} & & & & & & \\ & & & & & & & & \\ \hline Formate \\ absorption \\ band & Assignments \\ (range) & Nakamoto[4] & Saralidze et al. [5] \\ \hline \\ 1585-1600 & \nu_{asy}COO & & & & \\ & & & & & & \\ \hline 1360 & \nu_{sym}COO & & & & \\ \hline 1360 & \nu_{sym}COO & & & & \\ \hline 1360 & \nu_{sym}COO$	1545-1565	$\nu_{\rm asy} {\rm COO}$	$\nu_{\rm asy} \rm COO$	$\nu_{asy}COO$		
1425-1430 $\nu_{sym}COO$ $\nu_{sym}COO$ 1375-1377 ν_{c-c} $\delta_{sym}CH_3$ 1050-1057 ρ_rCH_3 ρ_rCH_3 1010-1020 ρ_rCH_3 ρ_rCH_3 935-948 ν_{cc} ν_{cc} 660-670 δ_{coo} σ_{coo} or π_{coo} 606-620 π_{CH} Formate absorption band Assignments (range) Nakamoto[4] Saralidze et al. [5] 1585-1600 $\nu_{asy}COO$ π_{cH} 1360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1360 $\nu_{sym}COO$ ν_{cH} 780 δ_{coo} π_{CH}	1440-1462	$\nu_{\rm sym} \rm COO$	$\delta_{asy}CH_3$	$\nu_{\rm sym} \rm COO$		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	1425-1430		$\nu_{\rm sym} \rm COO$	$\nu_{\rm sym} \rm COO$		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	1375–1377 1338–1345	$ \frac{\nu_{\rm C-C}}{\rho_{\rm r}\rm COO} $	$\delta_{sym}CH_3$			
935-948 ν_{CC} ν_{CC} ν_{CC} ν_{CC} 660-670 δ_{COO} δ_{COO} , or π_{COO} or π_{COO} σ_{CH} Formate absorption band Assignments band Assignments (range) Nakamoto[4] Saralidze et al.[5] 1585-1600 $\nu_{asy}COO$ $\nu_{asy}COO$ $\mu_{asy}COO$ 1400-1440 ρ_rCOO π_{CH} in-plane δ_{CH} 360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1360 $\nu_{sym}COO$ ν_{cH} π_{CH} 780 δ_{COO} π_{COO}	1050-1057 1010-1020	$ ho_{ m r} { m CH_3}$	$ ho_{ m r} { m CH}_3$			
$660-670$ δ_{COO} δ_{COO} , or π_{COO} σr σc_{CH} π_{CH} Formate absorption band Assignments π_{COO} $(range)$ Nakamoto[4] Saralidze et al.[5] 1585-1600 $\nu_{asy}COO$ $\nu_{asy}COO$ 1400-1440 ρ_rCOO π_{CH} in-plane δ_{CH} δ_{CH} 360 1360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1070 π_{COO} or π_{CH} π_{CH} 780 δ_{COO} π_{COO}	935-948	$\nu_{\rm CC}$	$\nu_{ m CC}$	$\nu_{\rm CC}$		
$\begin{array}{c} & & & & \\ & & & \\ \hline & & & \\ 606-620 & & & \\ \hline & & \\ Formate \\ absorption \\ band & Assignments \\ (range) & Nakamoto[4] & Saralidze et al.[5] \\ \hline \\ 1585-1600 & & \nu_{asy}COO \\ 1400-1440 & & \rho_rCOO & & \nu_{asy}COO \\ 1400-1440 & & \rho_rCOO & & & \\ \pi_{CH} & & \\ \hline \\ 1360 & & \nu_{sym}COO & & & \\ \nu_{sym}COO & & & & \\ \hline \\ 1360 & & \nu_{sym}COO & & & \\ \eta_{COO} & & & & \\ \pi_{CH} & & \\ \hline \\ 1360 & & & & \\ 780 & \delta_{COO} & & & \\ \hline \end{array}$	660-670	δ _{coo}	$\delta_{\rm COO}$,	$\pi_{ m COO}$		
$\begin{array}{c c} & \pi_{\rm COO} \\ \hline & \pi_{\rm CH} \end{array}$ Formate absorption band Assignments (range) Nakamoto[4] Saralidze et al.[5] $\begin{array}{c} 1585-1600 & \nu_{\rm asy}{\rm COO} & \nu_{\rm asy}{\rm COO} \\ 1400-1440 & \rho_{\rm r}{\rm COO} & \pi_{\rm CH} \text{ in-plane} \\ & \delta_{\rm CH} \\ 1360 & \nu_{\rm sym}{\rm COO} & \nu_{\rm sym}{\rm COO} \\ 1070 & \pi_{\rm COO} & \sigma_{\rm CH} & \pi_{\rm CH} \\ & 780 & \delta_{\rm COO} & \pi_{\rm COO} \end{array}$			or			
606-620 π_{CH} Formate absorption bandbandAssignments (range)Nakamoto[4]Saralidze et al.[5]1585-1600 $\nu_{asy}COO$ μ_{rCOO} 1400-1440 ρ_rCOO ν_{rCOO} π_{CH} 1360 $\nu_{sym}COO$ $\nu_{cym}COO$ 1070 π_{COO} π_{COO} 780 δ_{COO}			$\pi_{ m COO}$			
Formate absorption bandAssignments (range)1585-1600 $\nu_{asy}COO$ $\nu_{asy}COO$ 1585-1600 $\nu_{asy}COO$ $\nu_{asy}COO$ 1400-1440 ρ_rCOO π_{CH} in-plane δ_{CH} 1360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1070 π_{COO} or π_{CH} π_{CH} 780 δ_{COO} π_{COO}	606-620		$\pi_{ m CH}$			
bandAssignments(range)Nakamoto[4]Saralidze et al.[5]1585-1600 $\nu_{asy}COO$ $\nu_{asy}COO$ 1400-1440 ρ_rCOO π_{CH} in-plane δ_{CH} δ_{CH} 1360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1070 π_{COO} or π_{CH} π_{CH} 780 δ_{COO} π_{COO}	Formate absorption					
(range)Nakamoto[4]Saralidze et al.[5]1585-1600 $\nu_{asy}COO$ $\nu_{asy}COO$ 1400-1440 ρ_rCOO π_{CH} in-plane δ_{CH} δ_{CH} 1360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1070 π_{COO} or π_{CH} π_{CH} 780 δ_{COO} π_{COO}	band	Ass	Assignments			
$\begin{array}{ccccccc} 1585-1600 & \nu_{asy}COO & \nu_{asy}COO \\ 1400-1440 & \rho_{r}COO & \pi_{CH} \text{ in-plane} \\ & & & \\ & & \\ 1360 & \nu_{sym}COO & \nu_{sym}COO \\ 1070 & \pi_{COO} \text{ or } \pi_{CH} & \pi_{CH} \\ 780 & \delta_{COO} & & \pi_{COO} \end{array}$	(range)	Nakamoto[4]	Saralidze et al.[5]			
$1400-1440$ $\rho_r COO$ π_{CH} in-plane δ_{CH} δ_{CH} 1360 $\nu_{sym} COO$ 1070 π_{COO} or π_{CH} π_{CH} 780 δ_{COO}	1585-1600	$\nu_{asy}COO$	v _{asv} COO			
$ \begin{array}{c} \delta_{\rm CH} \\ 1360 & \nu_{\rm sym} \rm COO \\ 1070 & \pi_{\rm COO} \text{ or } \pi_{\rm CH} \\ 780 & \delta_{\rm COO} \end{array} \begin{array}{c} \nu_{\rm sym} \rm COO \\ \pi_{\rm COO} \end{array} $	1400-1440	ρ _r COO	π_{cu} in-plane			
1360 $\nu_{sym}COO$ $\nu_{sym}COO$ 1070 π_{COO} or π_{CH} π_{CH} 780 δ_{COO} π_{COO}		δ_{CH}	CH P			
1070 $\pi_{\rm COO}$ or $\pi_{\rm CH}$ $\pi_{\rm CH}$ 780 $\delta_{\rm COO}$ $\pi_{\rm COO}$	1360	$\nu_{\rm sym} \rm COO$	$\nu_{\rm sym} \rm COO$			
780 $\delta_{\rm COO}$ $\pi_{\rm COO}$	1070	$\pi_{ m COO}$ or $\pi_{ m CH}$	$\pi_{ m CH}$			
	780	$\delta_{\rm COO}$	$\pi_{ m COO}$			

Table 2. Previous assignments of mid i.r. absorptions in rare-earth acetates and formates*

*Note-Nakamoto's results based on sodium salts.

parison the absorptions for the sodium salts are included. It may be observed that the heavier rare-earth acetates and formates manifest absorptions at higher frequencies than the absorptions of the sodium salts, which have been assigned as ionic lattice modes. This is similar to the observations made in the low-frequency region for the anhydrous rare-earth carbonates[9] and nitrates[10]. The trend in the position of the strong vibrations appears to shift with increasing mass of the rare-earths (e.g., Eu < Tb < Er in the acetates and La < Nd in the formates) as expected for a metal-oxygen bond of high covalent character. These absorptions were found to be unaffected upon application of high external pressures and thus, demonstrated non-lattice like behavior. As a consequence, these absorptions are assigned to the metal-oxygen stretching vibrations. At least two such absorptions in a chelated-type structure. Contributing evidence comes from the separation of ν_{asym} COO and ν_{sym} COO vibrations. It would be expected that this

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Eu(OOCCH ₃) ₃	Eu(OOCCD ₃) ₃	Assignment	La(OOCH) ₃	La(OOCD) ₃	Assignment	
2980(w)		ν(CH)	2856(w)	band	ν(CH)	
2930(w)						
	2265(w)	ν(CD)		2208(w)	ν(CD)	
	2230(w)					
1542(vs)	1542(vs)	$\delta(COO)$ asym.	1605(vs)	1585(vs)	u(COO) asym	
1430(vs)		$\delta(CH_3)$ asym.	1580(vs)	1550(vs)J	v(coo) asym	
1410(sh)	1410(vs)	δ(COO) sym.	1428(vs) 1405(vs)		δ(CH)	
1340(m)		δ(CH ₃) sym.	1358(s)	1334(s) }	v(COO) sym.	
1230(w)				1056(m)	v(CD)	
1250(W)	1088(w)	S(CD.) asym	779(s)	770(m)	8(OCO)	
1050(m)	1000(w)	o(CD3) asym.	(1)(3)	//o(III)	0(000)	
1030(w)	1020(11)	S(CD) evm				
1019(m)	1030(w)	o(CD ₃) sym.				
1016(III) 050(III)		$\rho_r C \Pi_3$	262(0)	200(a ++ b+)		
950(W)	020()		202(8)	200(S, V. DI)	1 140	
942(w)	930(s)	$\nu_{\rm C-C}$	238(VS)		J	
	900(m)	00	1/7/ >			
	848(s)	$\rho_r CD_3$	16/(vs)			
(00)			150(m)			
680(m)		$\pi_{ m CH}$	121(s)			
668(m)						
644(sh)	640(s)]	Same				
614(m)	620(s)	0000				
	530(m)	$\pi_{\rm CD}$				
501(w)						
473(vw)	450(w), 430(w)					
266(s)	2(2(
220(m, sh)	202(VS, V. Dr)	$\nu_{\rm M-0}$				
205(vvw)	205(vvw)					
185(m)	1- Frit					
154(m)						

Table 3.	Assignments	for	Eu(OOCCH ₃) ₃ ,	$Eu(OOCCD_3)_3$	and	La(OOCH) ₃ ,	$La(OOCD)_3$	based on
			de	euteration studies				

Table 4. Low-frequency absorptions for several rare-earth acetates and formates

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Y(OAc) ₃	Eu(OAc) ₃	Tb(OAc) ₃	Er(OAc) ₃	Na(OAc)	La(OOCH) ₃	Nd(OOCH) ₃	Na(OOCH)
315(vs)	N. F. M. Th		ans while s	unades Fils	नार ता रहता	a or south of the	ne perort.
113021-21-1			292(sh)		262(s)	282(vs)	
260(m)	266(s)	276(s)	280(s)		238(vs)	240(vs)	
		258(w, sh)	260(w, sh)			183(w, sh)	
217(m)	220(sh)	225(w)	229(w)		167(s)		195(v. br)
	205(vvw)	205(vvw)		200(v. br)	150(m)	163(vs)	
165(sh)	185(m)	192(m)	194(m)				
156(m)	154(m)	160(m)	166(m)		121(m)	133(m)	
123(w)		133(w)	138(m)		0000-02180	and definition	
116(vw)		110(vw)					

Abbreviations: s = strong; m = medium; w = weak; v = very; br = broad; sh = shoulder.

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