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Magnetic Properties of Some Nickel(II)-Substituted Propanoate Dimers and the Crystal Structure of Tetrakis(μ-2-methyl-2-phenylpropionato-*O,O'*)bis(triphenylphosphine)dinickel(II), $[Ni(Me_2PhCCOO)_2PPh_3]_2$

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The dimeric Ni(II) complexes $[Ni(RCOO)_2L]_2$ (**1**, R = Me_2PhC, L = PPh_3; **2**, R = Me_2PhC, L = quinoline and **3**, R = Me_3C, L = 2-picoline) have been synthesized. They all display a dimer type of antiferromagnetism found in similar Cu(II) and Ni(II) complexes. The crystal structure of **1** has been determined from X-ray diffraction data at 295 K. The green crystals are triclinic with $a = 12.001(5)$, $b = 14.688(5)$, $c = 19.666(6)$ Å, $\alpha = 86.13(2)$, $\beta = 82.57(3)$, $\gamma = 76.718(3)$, $Z = 2$, space group $P\bar{1}$. Full-matrix least-squares refinement based on 5589 observed reflections gave a final $R = 0.085$. There are two crystallographically independent half molecules in the asymmetric unit. The compound has the classical dimeric structure well known for numerous Cu(II) carboxylates. Thus Ni(II) has a square-pyramidal five-coordination with P apical and Ni on average 0.276 Å above the basal oxygen plane. The Ni···Ni separations in the dimers average 2.759 Å.

Only relatively recently the first Ni(II) carboxylate dimers analogous to the Cu(II) carboxylate dimers have been synthesized and characterized by magnetic measurements and X-ray diffraction studies.[1–4] Magnetic susceptibility measurements of these compounds show an antiferromagnetic coupling, but the nature of the spin interaction has not been established with certainty. It is probably of the same type as that found in the corresponding Cu(II) dimers.[5] The present study is part of an effort to find a correlation between structure and magnetism in Ni(II) carboxylate dimers.

Experimental

Synthesis. $[Ni(Me_2PhCCOO)_2L]_2$ (L = PPh_3, **1**, quin, **2**) was prepared as follows. Nickel(II) acetate tetrahydrate (2 mmol), 2-methyl-2-phenylpropanoic acid (4 mmol), and L (2 mmol) were dissolved in 1-butanol (30 ml) by heating at ca. 80 °C, and this temperature was kept for 30 min. After filtration the solution was concentrated to ca. 2 ml by evaporation *in vacuo* with a bath temperature of ca. 80 °C. After adding 20 ml of *p*-xylene the solution was concentrated to ca. 5 ml. Petroleum ether (0.5 ml) was added to the solution and green crystals appeared after keeping at room temperature for 1 h. The crystals were collected and washed with a 1:1 mixture of petroleum ether and *p*-xylene, and dried *in vacuo* at room temperature. Yield: ca. 0.6 g. $[Ni(Me_3CCOO)_2(2\text{-pic})]_2$, **3**, was prepared by the same method and reported earlier.[6] Anal. **1**: Found: C, 70.66; H, 5.78; Ni, 9.00%. Calc. for $C_{76}H_{74}Ni_2O_8P_2$: C, 70.50; H, 5.76; Ni, 9.07%. **2**: Found: C, 68.07; H, 5.77; N, 2.65; Ni, 11.51%. Calc. for $C_{58}H_{58}N_2Ni_2O_8$: C, 67.72; H, 5.70; N, 2.72; Ni, 11.41%. **3**: Found: C, 54.38; H, 7.16; N, 3.94; Ni, 16.50%. Calc. for $C_{52}H_{58}N_2Ni_2O_8$: C, 54.27; H, 7.21; N, 3.94; Ni, 16.58%.

Structure determination. Some of the relevant data are shown in Table 1. Intensities were collected on an Enraf-

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Table 1. Crystal and experimental data.

Compound	$[Ni\{Me_2(Ph)CCOO\}_2PPh_3]_2$
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo*K*α
Wavelength/Å	0.70930
Crystal system	Triclinic
a/Å	12.001(5)
b/Å	14.688(5)
c/Å	19.666(6)
α/°	86.13(3)
β/°	82.57(3)
γ/°	76.72(3)
V/Å^3	3342.9
Space group	$P\bar{1}$
Formula wt.	1298.80
Z	2
*D*calc/gcm^{-3}	1.286
μ(Mo*K*α)/cm^{-1}	6.65
Crystal dimensions/mm	0.11×0.29×0.40
Scan mode/max θ/°	Omega/25
Fudge factor, *p*	0.020
Scale factor	2.973
No. independent measurements	11660
No. with $I > 2.5\sigma(I)$	5691
Absorption (max/min)	0.9283 and 0.8310
$R = \Sigma \lvert F_o - F_c \rvert / \Sigma F_o$	0.085
$R_w = [\Sigma w(F_o - F_c)^2 / \Sigma w F_o^2]^{1/2}$	0.083
$S = [\Sigma w(\Delta F)^2 / (N-n)]^{1/2}$	2.408

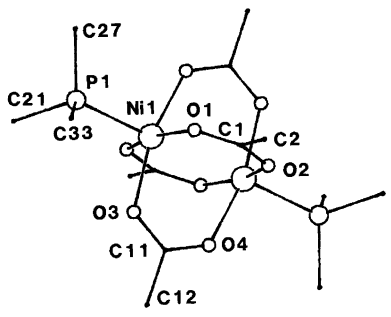
Nonius CAD-4 diffractometer at 295 K. The intensities of three standard reflections were checked every 2 h. Their intensities decreased 17.1% during intensity collection, and an appropriate scaling factor was applied. The data were also collected for Lorentz and polarization effects and for absorption. Unit-cell parameters are based on least-squares fits to the diffractometer settings of 25 general reflections. The structure was solved by conventional heavy-atom methods and refined by full-matrix least-squares methods minimizing $\Sigma w(\Delta F)$. During refinement, several reflections with low θ-values had relatively large ΔF-values. Refinement of some of the lighter atoms also was difficult. For these reasons, reflections with $\sin\theta/\lambda \leq 0.123$ (102 in all) were excluded from the final refinements. As a result, e.s.d. values of atomic parameters improved.

Because of the large number of parameters, only the Ni, P and O atoms were refined with anisotropic temperature factors. H atoms were placed in calculated positions (C–H = 0.95 Å) with isotropic temperature factors equal to 1.3 times those of the connected C atoms. Temperature factors of the phenyl groups, especially in the acid ligands, were high and some bond lengths and angles had unrealistic values, indicating possible disorder in these groups. This effect and the crystal decay is probably responsible for the high final *R*-factor of 0.085. The final difference map showed no maxima above 0.76 or below −0.57 e Å^{-3}. The choice of the space group $P1$ rather than the alternative $P\bar{1}$ was based on *E*-statistics and the result of the refinement of the structure. Computer programs used were supplied by Enraf-Nonius (SPD/VAX V3).

Magnetic measurement. Magnetic susceptibilities were determined in the temperature range 80–300 K by the Faraday method. The diamagnetic contribution was corrected using Pascal's constants. The results are shown in Fig. 3. The cryomagnetic data were analyzed with eqn. (1), (Fig. 3) which is derived from eqn. (2) by the simplification described below.

$$\chi_A = \frac{n(n+2)}{3}\frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1-P) + \frac{2}{3}\frac{Ng_{im}\beta^2}{kT}P + N\alpha \quad (1)$$

$$\chi_A = \frac{(n+2)}{3}\sum_{i=1}^{2n}\frac{Ng_i^2\beta^2}{3kT} \times \left[1+\frac{1}{3}\exp\left(\frac{-2J_i}{kT}\right)\right]^{-1} P_i + N\alpha \quad (2)$$



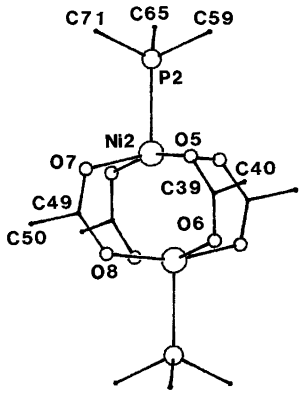


Fig. 1. The structures of the two crystallographically independent and centrosymmetric molecules of the dimer $[Ni(Me_2PhCCOO)_2PPh_3]_2$. Methyl and phenyl groups on the carboxylic ligands are omitted, the phenyl groups on PPh_3 are indicated by the C atoms bonded to P.

Table 2. Magnetic parameters.

Dimeric Ni(II) complex		χ–T data					Crystal data		
Carboxylate	L[a]	$-J$	g	$N\alpha$	P(%)	DI(%)	Space group	Z	Ref. etc.
Me_3CCOO	2,5-lu	126	2.00	400	1.72	0.67	$C2/c$	4	(2), (3)
$Me_2PhCCOO$	PPh_3	206	2.00	440	0.18	0.86	$P\bar{1}$	2	This work
$Me_2PhCCOO$	quin	142	2.03	450	1.34	1.31	$P2_1/n$	2	This work (3)
Me_3CCOO	2-pic	223	2.28	320	0.07	1.38	$P\bar{1}$	1	This work (3)
Me_3CCOO	2-Etpy	224	2.44	380	0.09	1.21	$P\bar{1}$	1	(2), (3)
Me_3CCOO	2,4-lu	180	2.71	400	0.22	0.54	$P\bar{1}$	1	(2) High-T
Me_3CCOO	2,4-lu	192	2.01	310	0.04	1.12	–	–	(2) Low-T

[a]lu, lutidine; quin, quinoline; pic, picoline; Etpy, ethylpyridine.

Table 3. Positional parameters and their estimated standard deviations.

Atom	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
Ni1	0.08004(9)	0.04021(8)	0.02332(6)	2.29(2)	C33	0.1414(7)	0.2528(6)	0.0639(5)	3.1(2)*
Ni2	0.3891(1)	0.51036(9)	0.53295(6)	2.85(3)	C34	0.1856(9)	0.3239(8)	0.0290(6)	5.2(3)*
P1	0.2060(2)	0.1288(2)	0.0569(1)	2.58(5)	C35	0.133(1)	0.4171(8)	0.0421(6)	6.4(3)*
P2	0.2200(2)	0.5187(2)	0.6132(1)	3.62(6)	C36	0.035(1)	0.4390(8)	0.0858(6)	5.8(3)*
O1	0.0073(5)	0.1472(4)	−0.0365(3)	3.7(2)	C37	−0.010(1)	0.3718(8)	0.1204(6)	5.7(3)*
O2	−0.1244(5)	0.0844(4)	−0.0722(3)	3.9(2)	C38	0.0426(9)	0.2773(7)	0.1096(5)	4.5(2)*
O3	−0.0453(5)	0.0811(4)	0.1002(3)	3.7(2)	C39	0.5802(8)	0.3578(6)	0.5769(5)	3.2(2)*
O4	−0.1734(5)	0.0189(4)	0.0610(3)	3.9(2)	C40	0.6211(9)	0.2756(7)	0.6256(5)	4.4(2)*
O5	0.4758(5)	0.3962(5)	0.5822(3)	4.2(2)	C41	0.520(1)	0.256(1)	0.6758(8)	9.4(4)*
O6	0.6575(5)	0.3810(5)	0.5348(3)	4.5(2)	C42	0.699(2)	0.305(1)	0.668(1)	12.2(5)*
O7	0.3652(5)	0.4234(5)	0.4645(3)	4.4(2)	C43	0.682(1)	0.188(1)	0.5876(8)	10.1(4)*
O8	0.5451(5)	0.4053(4)	0.4146(3)	3.7(2)	C44	0.801(2)	0.146(1)	0.601(1)	14.3(6)*
C1	−0.0762(8)	0.1505(6)	−0.0703(5)	3.2(2)*	C45	0.859(2)	0.054(2)	0.562(1)	17.7(8)*
C2	−0.1225(8)	0.2443(7)	−0.1088(5)	3.8(2)*	C46	0.790(2)	0.034(2)	0.526(1)	16.0(7)*
C3	−0.156(1)	0.2208(8)	−0.1773(6)	5.5(3)*	C47	0.686(2)	0.057(2)	0.512(1)	19.0(9)*
C4	−0.025(1)	0.2983(8)	−0.1255(6)	6.0(3)*	C48	0.618(2)	0.157(1)	0.551(1)	14.1(6)*
C5	−0.2195(8)	0.2970(7)	−0.0634(5)	4.2(2)*	C49	0.4464(8)	0.3860(6)	0.4233(5)	3.6(2)*
C6	−0.331(1)	0.3199(9)	−0.0792(7)	7.9(4)*	C50	0.4312(8)	0.3117(7)	0.3756(5)	3.9(2)*
C7	−0.421(1)	0.371(1)	−0.0303(9)	11.1(5)*	C51	0.342(1)	0.2603(8)	0.4136(6)	5.6(3)*
C8	−0.393(1)	0.394(1)	0.0257(8)	10.3(5)*	C52	0.544(1)	0.2440(9)	0.3583(7)	7.2(3)*
C9	−0.284(1)	0.381(1)	0.0436(8)	10.4(5)*	C53	0.3835(8)	0.3633(7)	0.3127(5)	4.3(2)*
C10	−0.198(1)	0.3272(9)	−0.0025(7)	7.8(4)*	C54	0.286(1)	0.423(1)	0.3149(8)	9.3(4)*
C11	−0.1439(7)	0.0639(6)	0.1034(4)	3.0(2)*	C55	0.235(2)	0.470(1)	0.254(1)	13.5(6)*
C12	−0.2302(8)	0.1002(6)	0.1641(5)	3.7(2)*	C56	0.290(1)	0.454(1)	0.1954(7)	8.6(4)*
C13	−0.205(1)	0.1842(8)	0.1933(6)	5.8(3)*	C57	0.389(1)	0.391(1)	0.1892(8)	9.3(4)*
C14	−0.350(1)	0.1316(9)	0.1367(7)	7.4(3)*	C58	0.446(1)	0.3414(9)	0.2469(7)	7.6(3)*
C15	−0.231(1)	0.0248(9)	0.2153(6)	6.9(3)*	C59	0.2536(8)	0.4743(7)	0.6986(5)	3.9(2)*
C16	−0.141(2)	−0.022(1)	0.238(1)	13.2(6)*	C60	0.333(1)	0.5099(8)	0.7263(6)	5.7(3)*
C17	−0.140(2)	−0.109(2)	0.297(1)	18.2(8)*	C61	0.360(1)	0.4785(8)	0.7925(6)	6.8(3)*
C18	−0.243(2)	−0.117(2)	0.310(1)	16.6(8)*	C62	0.312(1)	0.4130(8)	0.8281(6)	6.6(3)*
C19	−0.344(2)	−0.062(2)	0.301(1)	16.8(8)*	C63	0.237(1)	0.3766(9)	0.8014(7)	7.4(3)*
C20	−0.340(2)	0.009(1)	0.2450(9)	11.7(5)*	C64	0.206(1)	0.4063(8)	0.7335(6)	6.4(3)*
C21	0.2524(7)	0.0988(6)	0.1407(4)	2.6(2)*	C65	0.1322(9)	0.6333(7)	0.6312(5)	4.5(2)*
C22	0.2275(8)	0.0206(7)	0.1763(5)	4.2(2)*	C66	0.1488(9)	0.7099(8)	0.5924(6)	5.3(3)*
C23	0.2578(9)	−0.0036(7)	0.2429(6)	5.2(3)*	C67	0.083(1)	0.799(1)	0.6048(7)	8.3(4)*
C24	0.3132(9)	0.0516(7)	0.2723(5)	4.9(2)*	C68	−0.008(1)	0.809(1)	0.6573(7)	8.4(4)*
C25	0.3369(9)	0.1279(7)	0.2398(5)	4.5(2)*	C69	−0.025(1)	0.7364(9)	0.6944(7)	7.8(4)*
C26	0.3056(8)	0.1554(7)	0.1733(5)	4.2(2)*	C70	0.040(1)	0.6453(9)	0.6837(6)	6.9(3)*
C27	0.3343(8)	0.1271(6)	−0.0033(5)	3.2(2)*	C71	0.1261(8)	0.4464(7)	0.5900(5)	3.9(2)*
C28	0.4415(9)	0.1178(7)	0.0140(5)	4.7(2)	C72	0.176(1)	0.3572(8)	0.5708(6)	5.6(3)*
C29	0.535(1)	0.1214(8)	−0.0372(6)	5.9(3)*	C73	0.112(1)	0.2963(9)	0.5518(7)	7.6(3)*
C30	0.514(1)	0.1371(8)	−0.1032(6)	5.8(3)*	C74	−0.004(1)	0.3341(9)	0.5513(7)	7.5(3)*
C31	0.407(1)	0.1469(8)	−0.1233(6)	6.4(3)*	C75	−0.056(1)	0.4191(8)	0.5677(6)	6.4(3)*
C32	0.3156(9)	0.1406(7)	−0.0729(5)	4.9(2)*	C76	0.007(1)	0.4802(8)	0.5880(6)	5.8(3)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)^* [a^2{*}B(1,1)+b^2{*}B(2,2)+c^2{*}B(3,3)+ab(\cos\gamma){*}B(1,2)+ac(\cos\beta){*}B(1,3)+bc(\cos\alpha){*}B(2,3)]$.

Eqn. (2) is a modified expression of a channel model developed by Rakitin *et al.*,[7] where n is the number of unpaired electrons on one metal ion ($n = 2$ for the Ni^{2+}–Ni^{2+} dimer), P_i is the mole fraction of each component, and the other symbols have their usual meanings. For the unpaired electrons in the dimeric molecule $i = 1,\cdots n$, and for the electrons in the monomeric impurity $i = n+1,\cdots 2n$ and $J_{n+1},\cdots J_{2n} = 0$. When the values of $g(g_1 = g_2 = g)$ and $J(J_1 = J_2 = J)$ for the dimeric unit and those of $g_{im}(g_3 = g_4 = g_{im})$, $J_3 = J_4 = 0$, and $P(P_3 = P_4 = P)$ for the paramagnetic impurity are used, eqn. (1) is obtained. The best-fit parameters for g, J, P and $N\alpha$ were obtained by a nonlinear least-squares fitting procedure assuming $g_{im} = 2.2$. The quality of fit was estimated by means of the discrepancy index, $\sigma_{dis} = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi^2{}_{obs}]^{1/2}$. The values of the magnetic parameters are summarized in Table 2 together with some crystallographic data.

Results and discussion

Magnetic parameters are listed in Table 2, atomic positional parameters in Table 3, bond distances and angles in Tables 4 and 5 and molecular planes in Table 6. Further details of the crystal structure work are deposited with the Cambridge Crystallographic Data Centre, UK.

Molecular structure. The structures of the two crystallographically independent and centrosymmetric molecules **1a** and **1b** are shown in Fig. 2. They are quite similar. The carboxylate ligands are all bridging and the dimers have the cage structure well known from the Cu(II) carboxylate dimers with a somewhat distorted square-pyramidal coordination of the metal atom. The PPh_3 group is apical, while four oxygen atoms form the basal plane. The main difference between the two molecules is represented by the Ni′–Ni–P angles, which are 172.43(7) and 166.65(6)° for **1a** and **1b**. They agree with those of other dimeric Ni(II) carboxylates, but the angle in **1a** is a bit high.[1–3] Figure 3 shows the packing of molecules in the unit cell. No short intermolecular distances were found.

Bonding. The Ni–Ni distances for **1a** and **1b** are 2.752(1) and 2.765(2) Å, respectively, and may be compared to distances in the range 2.708–2.765 found earlier for such compounds.[1–3] The distances are too large for a Ni–Ni

Table 4. Bond lengths with estimated standard deviations (in Å).

Ni1–Ni1′[a]	2.752(1)	C8–C9	1.37(1)	C43–C44	1.46(2)
*a*Ni1–P1	2.386(2)	C9–C10	1.41(1)	C43–C48	1.28(2)
Ni1–O1	2.001(4)	C11–C12	1.514(8)	C44–C45	1.56(2)
Ni1–O2′	2.001(4)	C12–C13	1.501(9)	C45–C46	1.25(2)
Ni1–O3	2.008(4)	C12–C14	1.56(1)	C46–C47	1.28(2)
Ni1–O4′	2.006(4)	C12–C15	1.45(1)	C47–C48	1.69(2)
Ni2–Ni2′	2.765(2)	C15–C16	1.26(1)	C49–C50	1.542(9)
Ni2–P2	2.389(2)	C15–C20	1.42(1)	C50–C51	1.540(9)
Ni2–O5	2.017(4)	C16–C17	1.67(2)	C50–C52	1.50(1)
Ni2–O6′	2.032(4)	C17–C18	1.26(2)	C50–C53	1.512(9)
Ni2–O7	2.007(4)	C18–C19	1.32(2)	C53–C54	1.29(1)
Ni2–O8′	2.014(4)	C19–C20	1.47(2)	C53–C58	1.43(1)
P1–C21	1.802(6)	C21–C22	1.376(8)	C54–C55	1.47(2)
P1–C27	1.813(6)	C21–C26	1.388(8)	C55–C56	1.27(1)
P1–C33	1.815(6)	C22–C23	1.406(9)	C56–C57	1.33(1)
P2–C59	1.822(7)	C23–C24	1.357(9)	C57–C58	1.46(1)
P2–C65	1.800(7)	C24–C25	1.322(9)	C59–C60	1.372(9)
P2–C71	1.832(7)	C25–C26	1.414(9)	C59–C64	1.366(9)
O1–C1	1.262(7)	C27–C28	1.348(8)	C60–C61	1.40(1)
O2–C1	1.243(7)	C27–C32	1.409(9)	C61–C62	1.34(1)
O3–C11	1.259(7)	C28–C29	1.416(9)	C62–C63	1.33(1)
O4–C11	1.232(7)	C29–C30	1.35(1)	C63–C64	1.45(1)
O5–C39	1.245(7)	C30–C31	1.37(1)	C65–C66	1.355(9)
O6–C39	1.253(7)	C31–C32	1.391(9)	C65–C70	1.40(1)
O7–C49	1.231(7)	C33–C34	1.381(8)	C66–C67	1.38(1)
O8–C49	1.268(7)	C33–C38	1.384(8)	C67–C68	1.40(1)
C1–C2	1.548(8)	C34–C35	1.40(1)	C68–C69	1.29(1)
C2–C3	1.539(9)	C35–C36	1.34(1)	C69–C70	1.40(1)
C2–C4	1.548(9)	C36–C37	1.34(1)	C71–C72	1.364(9)
C2–C5	1.470(9)	C37–C38	1.404(9)	C71–C76	1.404(9)
C5–C10	1.38(1)	C39–C40	1.519(9)	C72–C73	1.40(1)
C5–C6	1.37(1)	C40–C41	1.53(1)	C73–C74	1.38(1)
C6–C7	1.45(1)	C40–C42	1.49(1)	C74–C75	1.30(1)
C7–C8	1.28(1)	C40–C43	1.52(1)	C75–C76	1.41(1)

[a] Atoms marked with a prime are related to those of Table 3 by molecular symmetry centres.

Table 5. Bond angles with estimated standard deviations/°.

Ni1′–Ni1–O1[a]	81.3(1)	Ni1–O1–C1	126.8(4)	P1–C21–C22	119.3(5)	O7–C49–C50	120.3(7)
Ni1′–Ni1–O2′	83.1(1)	Ni1′–O2–C1	125.0(4)	P1–C21–C26	122.4(5)	O8–C49–C50	114.7(6)
Ni1′–Ni1–O3	84.0(1)	Ni1–O3–C11	123.1(4)	C22–C21–C26	118.1(6)	C49–C50–C51	107.8(6)
Ni1′–Ni1–O4′	80.2(1)	Ni1′–O4–C11	128.6(4)	C21–C22–C23	121.4(6)	C49–C50–C52	110.1(6)
Ni1′–Ni1–P1	172.43(7)	Ni2–O5–C39	131.1(4)	C22–C23–C24	118.9(6)	C49–C50–C53	107.2(5)
P1–Ni1–O1	91.3(1)	Ni2′–O6–C39	118.3(4)	C23–C24–C25	121.1(8)	C51–C50–C52	110.2(6)
P1–Ni1–O2′	104.4(1)	Ni2–O7–C49	120.2(4)	C24–C25–C26	121.5(6)	C51–C50–C53	108.8(6)
P1–Ni1–O3	94.9(1)	Ni2′–O8–C49	130.1(4)	C21–C26–C25	118.9(7)	C52–C50–C53	112.5(6)
P1–Ni1–O4′	101.0(1)	O1–C1–O2	123.8(6)	C28–C27–C32	119.6(6)	C50–C53–C54	123.5(8)
O1–Ni1–O2′	164.3(2)	O2–C1–C2	119.3(6)	P1–C27–C28	125.1(5)	C50–C53–C58	118.7(7)
O1–Ni1–O3	90.2(2)	O1–C1–C2	116.9(6)	P1–C27–C32	115.3(5)	C54–C53–C58	117.8(8)
O1–Ni1–O4′	88.6(2)	C1–C2–C3	107.5(5)	C27–C28–C29	120.5(7)	C53–C54–C55	124(1)
O2′–Ni1–O3	89.6(2)	C1–C2–C4	109.4(6)	C28–C29–C30	118.4(8)	C54–C55–C56	119(1)
O2′–Ni1–O4′	87.3(2)	C1–C2–C5	107.0(5)	C29–C30–C31	123.2(8)	C55–C56–C57	120(1)
O3–Ni1–O4′	164.1(2)	C3–C2–C4	107.6(6)	C30–C31–C32	118.0(8)	C56–C57–C58	125(1)
Ni2′–Ni2–O5	77.4(2)	C3–C2–C5	113.8(6)	C27–C32–C31	120.3(7)	C53–C58–C57	114.5(8)
Ni2′–Ni2–O6′	87.0(1)	C4–C2–C5	111.4(6)	C34–C33–C38	118.0(6)	P2–C59–C60	117.0(6)
Ni2′–Ni2–O7	86.5(1)	C2–C5–C10	118.8(7)	P1–C33–C34	124.9(5)	P2–C59–C64	122.4(5)
Ni2′–Ni2–O8′	77.8(1)	C2–C5–C6	123.4(7)	P1–C33–C38	117.0(5)	C60–C59–C64	120.6(7)
Ni2′–Ni2–P2	166.65(6)	C6–C5–C10	117.8(8)	C33–C34–C35	119.8(7)	C59–C60–C61	118.7(7)
P2–Ni2–O5	92.3(1)	C5–C6–C7	119.0(9)	C34–C35–C36	121.0(7)	C60–C61–C62	121.5(8)
P2–Ni2–O6′	103.6(1)	C6–C7–C8	119(1)	C35–C36–C37	120.8(9)	C61–C62–C63	120.4(8)
P2–Ni2–O7	101.6(1)	C7–C8–C9	126(1)	C36–C37–C38	119.8(8)	C62–C63–C64	120.6(9)
P2–Ni2–O8′	94.1(1)	C8–C9–C10	114(1)	C33–C38–C37	120.6(7)	C59–C64–C63	118.2(8)
O5–Ni2–O6′	164.1(2)	C5–C10–C9	123.5(9)	O5–C39–O6	125.9(7)	P2–C65–C66	121.4(6)
O5–Ni2–O7	87.2(2)	O3–C11–O4	124.1(6)	O5–C39–C40	118.7(6)	P2–C65–C70	120.7(6)
O5–Ni2–O8′	90.9(2)	O3–C11–C12	117.2(6)	O6–C39–C40	115.4(6)	P2–C71–C72	117.9(6)
O6′–Ni2–O7	88.7(2)	O4–C11–C12	118.6(6)	C39–C40–C41	110.3(7)	P2–C71–C76	122.9(6)
O6′–Ni2–O8′	88.9(2)	C11–C12–C13	112.4(6)	C39–C40–C42	106.9(7)	C66–C65–C70	117.8(7)
O7–Ni2–O8′	164.2(2)	C11–C12–C14	106.6(6)	C39–C40–C43	112.2(7)	C65–C66–C67	123.0(8)
Ni1–P1–C21	115.7(2)	C11–C12–C15	108.6(6)	C41–C40–C42	105.7(8)	C66–C67–C68	117.8(9)
Ni1–P1–C27	114.0(2)	C13–C12–C14	107.4(6)	C41–C40–C43	110.4(7)	C67–C68–C69	120(1)
Ni1–P1–C33	113.7(2)	C13–C12–C15	111.4(6)	C42–C40–C43	111.1(9)	C68–C69–C70	124(1)
C21–P1–C27	107.3(3)	C14–C12–C15	110.4(7)	C40–C43–C44	117(1)	C65–C70–C69	117.7(8)
C21–P1–C33	101.5(3)	C12–C15–C16	123(1)	C40–C43–C48	114(1)	C72–C71–C76	119.1(7)
C27–P1–C33	103.2(3)	C12–C15–C20	118(1)	C44–C43–C48	128(1)	C71–C72–C73	122.5(8)
Ni2–P2–C59	112.3(2)	C16–C15–C20	119(1)	C43–C44–C45	115(1)	C72–C73–C74	115.2(9)
Ni2–P2–C65	117.2(2)	C15–C16–C17	124(1)	C44–C45–C46	110(2)	C73–C74–C75	125.1(9)
Ni2–P2–C71	112.5(2)	C16–C17–C18	106(2)	C45–C46–C47	143(2)	C74–C75–C76	119.9(9)
C59–P2–C65	101.4(3)	C17–C18–C19	134(2)	C46–C47–C48	109(2)	C71–C76–C75	118.1(7)
C59–P2–C71	104.4(3)	C18–C19–C20	115(2)	C43–C48–C47	114(1)		
C65–P2–C71	107.8(3)	C15–C20–C19	119(1)	O7–C49–O8	125.0(7)		

[a] Atoms marked with a prime are related to those at Table 3 by molecular symmetry centres.

bond;[1,2] also the displacement at each Ni atom from the basal O_4 plane is in a direction away from the other Ni atom in the dimers [0.274(1) Å for Ni 1 and 0.277(1) Å for Ni 2]. Average Ni–O bond lengths of 2.004(4) Å for **1a** and 2.018(11) Å for **1b** fall within the range for such bonds found earlier.[1–3] The apical Ni–P bond lengths are Ni1–P1 = 2.386(2) and Ni2–P2 = 2.389(2) Å, which are marginally longer than 2.368(1) Å found for the corre-

Table 6. Least-squares planes in the molecules.

No. of plane	Atoms in plane	Δ/Å[a]	Distance to other atoms/Å	Interplanar angles
1	O1, O2′, O3, O4′	0.003	Ni1 0.274	1,2 119.0(1)
2	O5, O6′, O7, O8′	0.001	Ni2 0.277	3,4 89.7(1)
3	Ni1, O1, C1, O2, Ni1′	0.018	P1 −0.082	5,6 88.0(1)
4	Ni1, O3, C11, O4, Ni1′	0.015	P1 0.339	
5	Ni2, O5, C39, O6, Ni2′	0.037	P2 −0.419	
6	Ni2, O7, C49, O8, Ni2′	0.038	P2 −0.485	

[a] Max. deviation from plane.

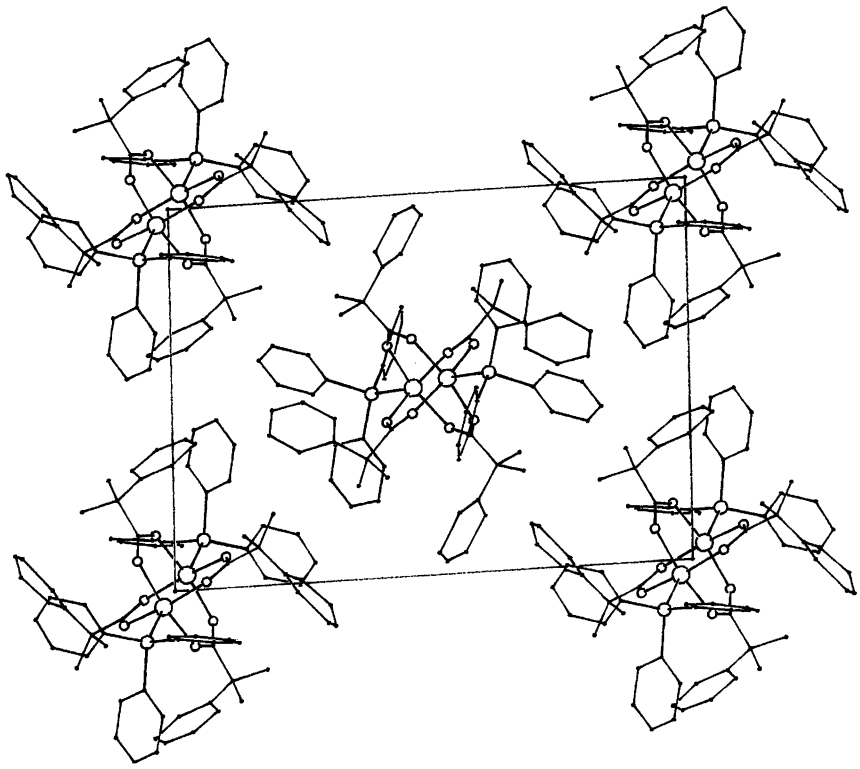


Fig. 2. The packing of the molecules in the unit cell as seen in the projection along the *a*-axis.

sponding bond length in $[Ni(MePh_2SiCOO)_2PPh_3]_2$.[3] The average dimensions of the bridging carboxyl groups in the dimers are C=O = 1.249(13) Å, C_{sp^2}–C_{sp^3} = 1.531(17) Å, ∠O–C–O = 124.7(9)°. Average total length of the Ni–O–C–O–Ni′ bridges is 6.545 Å.

Magnetic properties. The magnetic susceptibility data observed for the present compounds could not be fitted well to the Van Vleck equation, eqn. (3), for the coupling system of two $S = 1$ spin states.

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left(\frac{5 + \exp\left(\frac{-4J}{kT}\right)}{5 + 3\exp\left(\frac{-4J}{kT}\right) + \exp\left(\frac{-6J}{kT}\right)}\right) \times (1 - P) + \frac{2}{3}\frac{Ng_{im}^2\beta^2}{kT}P + N\alpha \qquad (3)$$

However, as previously reported for the same type of Ni(II) dimers, a good fit for eqn. (4) was obtained for the magnetic data (Fig. 3).[2]

$$\chi_A = 2\frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp\left(\frac{-2J}{kT}\right)\right]^{-1}(1 - P) + \frac{2Ng_{im}^2\beta^2}{3kT}P + N\alpha \qquad (4)$$

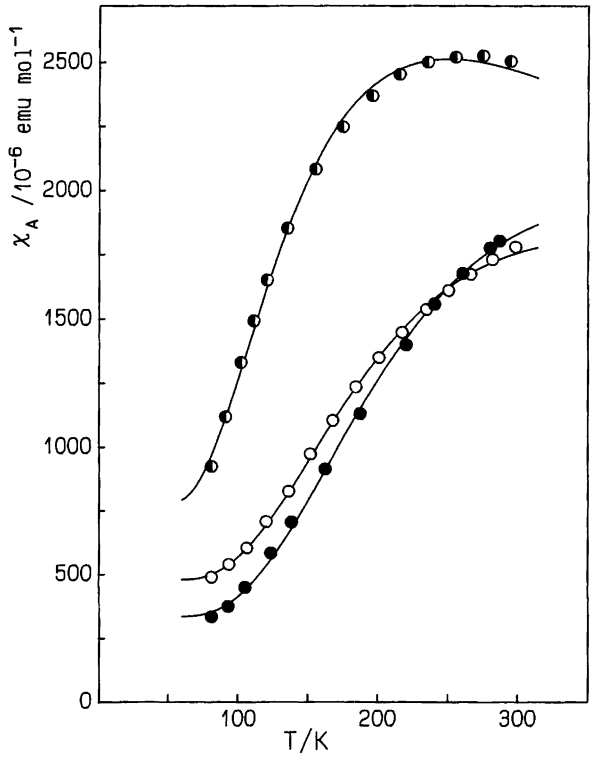


Fig. 3. Variation of magnetic susceptibility for some Ni(II) carboxylate dimers. ◐, $[Ni(Me_2PhCCOO)_2(quin)]_2$; ○, $[Ni(Me_2PhCCOO)_2PPh_3]_2$; ●, $[Ni(Me_3CCOO)_2(2\text{-pic})]_2$.

The g-values in the previous report, however, were much larger than 2.2. The reason for this trend is apparent from the comparison between the $J = 0$ extreme of eqns. (4) and (5):

$$\chi_A = \frac{Ng^2\beta^2 S(S+1)}{3kT} = \frac{n(n+2)}{3}\,\frac{Ng^2\beta^2}{4kT} \qquad (5)$$

where S is the total quantum number and n is the number of unpaired electrons per metal ion. The expression indicates that the contribution of each electron to the magnetic susceptibility increases by $(n+2)/3$ owing to intra-atomic interaction of electronic spins. If the eqn. (4) type of treatment is possible, the general equation for a system with n unpaired electrons per metal ion must be

$$\chi_A = \frac{(n+2)}{3}\sum_{i=1}^{n}\frac{Ng_i^2\beta^2}{3kT} \times\left[1+\frac{1}{3}\exp\left(\frac{-2J_i}{kT}\right)\right]^{-1} + N\alpha \qquad (6)$$

When paramagnetic impurity is included in the expression, eqn. (6) is converted into eqn. (2). When g is parametrized, a comparison of eqn. (2) with eqn. (4) gives the relation $g = (4/3)^{1/2} g_i$. For the application of eqn. (2), a single g-value for the electrons on the dimeric unit and a single g_{im}-value of the usual paramagnetic Ni(II) unit were used. This was done to avoid unreasonable convergence at the least-squares parameter fitting.

The g-values for $[Ni(Me_3CCOO)_2(2.5\text{-lu})]_2$, $[Ni(Me_2PhCCOO)_2PPh_3]_2$, $[Ni(Me_3CCOO)_2(2.4\text{-lu})]_2$, in the low-$T$ region ($T<200$ K), and $[Ni(Me_2PhCCOO)_2(quin)]_2$[2,3] are 2.00, 2.00, 2.01 and 2.03, respectively. Those for $[Ni(Me_3CCOO)_2(2\text{-pic})]_2$,[3] $[Ni(Me_3CCOO)_2(2\text{-Etpy})]_2$[2,3] and $[Ni(Me_3CCOO)_2(2.4\text{-lu})]_2$[2] in the high-$T$ region ($T>200$ K) are 2.28, 2.44 and 2.71, respectively. Thus, these compounds can be grouped by their g-values:

Group I for the compounds with g-values close to 2, and Group II for the compounds with larger g-values. The independent molecules of $[Ni(Me_2PhCCOO)_2PPh_3]_2$ which belong to Group I show no significant structural difference compared to each other or even to the structure of $[Ni(Me_3CCOO)_2(2.4\text{-lu})]_2$ (high-T) which belongs to Group II. The values of the exchange integrals, $-J$, were in the range of 126–224 cm^{-1}, as shown in Table 2. The $-J$-values are comparable to those determined by Novotortsev *et al.*[6] for $[Ni(Me_3CCOO)_2L]_2$ (L = 2-pic, 4-pic, quin, and PPh_3; $-J = 150$–157 cm^{-1}). Since Novotortsev *et al.* showed no χ_A equation for the magnetic analysis, the magnetic property of $[Ni(Me_3CCOO)_2(2\text{-pic})]_2$ was reinvestigated for comparison; the result is included in Table 2. For the compounds listed in Table 2, no apparent correlation was found between their magnetic and structural properties. The only apparent difference in the two groups (I and II) is found in their molecular packing. At present, however, there are not enough data for further discussion. A wide range of magneto-crystal data are required to elucidate the mechanism of magnetic interaction in Ni(II) carboxylate dimers. In addition there is another problem to be solved. Since eqn. (4) is identical with the equation for spin equilibrium of the monomeric Ni(II) compound, a fit of χ–T data to eqn. (4) does not unequivocally lead to a spin–spin interaction between the two metal atoms in the dimeric unit. In order to reveal the non-existence of a monomeric spin equilibrium in this series of compounds, studies on Ni^{2+}–Zn^{2+} heteronuclear carboxylate complexes are in progress. At present, although the purity of the Ni^{2+}–Zn^{2+} dimer is not sufficient, the partial paramagnetic behaviour of the Ni^{2+}–Ni^{2+}, Ni^{2+}–Zn^{2+}, and Zn^{2+}–Zn^{2+} mixtures suggests the non-existence of monomeric spin equilibrium on the Ni^{2+} ion in the Ni^{2+}–Zn^{2+} dimer.

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