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Heterometallic Co^{II}-Li^{I} carboxylate complexes with N-heterocyclic carbene, triphenylphosphine and pyridine: a comparative study of magnetic properties

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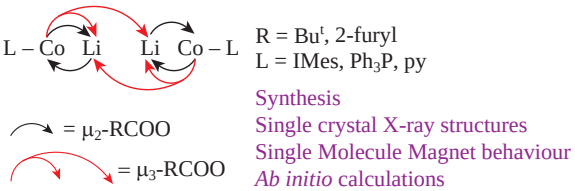
Heterometallic Co^{II}-Li^{I} compounds with N-heterocyclic carbene 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), triphenylphosphine (Ph_3P) and pyridine (py), $[Co_2Li_2(Piv)_6(IMes)_2]$ (Piv is the anion of pivalic acid), $[Co_2Li_2(Piv)_6(Ph_3P)_2]$ and $[Co_2Li_2(Fur)_6(py)_2]$ (Fur is the anion of 2-furoic acid), respectively, have been prepared and structurally characterized by X-ray crystallography. Easy-plane magnetic anisotropy in Co^{II} complexes with pseudo-tetrahedral cores CoO_3X (X = C, P and N) was revealed by measuring the magnetic properties together with quantum-chemical calculations using the SA-CASSCF/NEVPT2 approach. The field-induced slow magnetic relaxation of the complexes was mainly attributed to the Raman and direct processes.



Keywords: *ab initio* calculations, cobalt(II), easy-plane magnetic anisotropy, heterometallic carboxylate complexes, N-heterocyclic carbenes, single molecule magnet.

N-Heterocyclic carbenes (NHC) are very attractive ligands in modern coordination and organometallic chemistry.[1] Most publications describe the catalytic activity of NHC complexes,[2,3] while other functional properties such as luminescence,[4,5] bioactivity[6] and magnetism[7] are often overshadowed. It has recently been found that linear NHC-containing Co^{II} complexes are highly efficient single-molecule magnets (SMMs).[8] One of them currently holds the second-highest spin-reversal barrier record among transition metal SMMs.[9,10] Despite this, the systematic use of NHC ligands to create new magnetoactive compounds is not common.[11–14] On the other hand, carboxylate ligands are uniquely suited for molecular magnetism studies, and they have been widely used to develop new SMMs.[15–20] At the same time, however, carboxylate complexes with NHCs as ancillary ligands are reported in a limited number of publications.[21,22]

Here we report on the synthesis, structural and magnetic studies of two heterometallic carboxylate complexes $[Co_2Li_2(Piv)_6(L)_2]$ [Piv is the anion of pivalic acid, L is 1,3-bis(2,4,6-trimethylphenyl) imidazol-2-ylidene (IMes) or triphenylphosphine (PPh_3)]. The purpose of changing the ancillary ligand was to trace how the structures and magnetic properties of the polynuclear carboxylate core are affected by ligands with different donor strengths. In addition, it is known that introducing a heavier atom (such as P) into the coordination sphere of Co^{II} improves its magnetic anisotropy.[23,24] To raise the level of discussion, we also used the structural and magnetic data for the previously described complexes $[Co_2Li_2(Piv)_6(py)_2]$ **3** (py is pyridine)[25] and $[Co_2Li_2(Piv)_6(lut)_2]$ **4** (lut is 2,4-lutidine).[26] Besides, we deliberately synthesized a new complex $[Co_2Li_2(Fur)_6(py)_2]$ **5** (Fur is the anion of 2-furoic acid), which was used as an independent structural model containing carboxylate anions other than pivalate.

Compound **1** was synthesized by exchanging pyridine for IMes (Schemes 1 and S1[†]) according to the synthesis protocol recently developed for 3*d*–4*f* metal carboxylates containing

$$[Co_2Li_2(Piv)_6(Py)_2] + 2IMes \xrightarrow[-2py]{} [Co_2Li_2(Piv)_6(IMes)_2]$$
1 (72%)

$$\{Co(Piv)_2\} + Li(Piv) + Ph_3P \longrightarrow 1/2[Co_2Li_2(Piv)_6(Ph_3P)_2]$$
2 (93%)

$$\{Co(Piv)_2\} + Li(Piv) + 3HFur + py \xrightarrow[-3HPiv]{} 1/2[Co_2Li_2(Fur)_6(py)_2]$$
5 (84%)

Scheme 1

[†] For details, see Online Supplementary Materials.

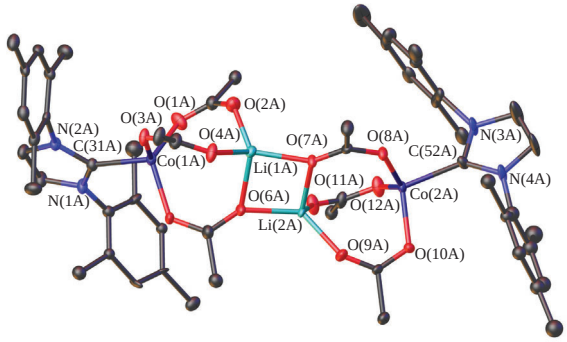


Figure 1 Molecular structure of molecule **A** in the crystal lattice of compound **1**. Methyl substituents of pivalate groups, hydrogen atoms and disordered fragments are omitted for clarity.

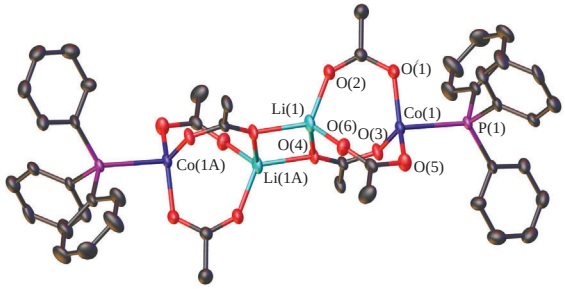


Figure 2 Molecular structure of compound **2**. Methyl substituents of pivalate groups and hydrogen atoms are omitted for clarity.

NHC as ancillary ligand.[22] Complexes **2** and **5** were obtained by one-pot synthesis starting from Co and Li pivalates.

Complexes **1** (Figure 1) and **2** (Figure 2) crystallize in the triclinic space group $P\bar{1}$.‡ The asymmetric unit of compound **1** contains two independent noncentrosymmetric structurally similar molecules. The molecule **2** is centrosymmetric with the inversion center at the intersection of the diagonals of the almost square O_2Li_2 moiety.

The molecules of complexes **1** and **2** consist of two identical fragments {CoLi(Piv)$_3$(L)}, in which the Co ions are coordinated by the P atom of Ph_3P in complex **2** or the C atom of IMes in complex **1**. Three carboxylate bridges link Co^{II} and Li^{I} ions. Two Piv anions have a μ_2-bridging type of coordination, and the third has a μ_3-bridging type of coordination and binds two Li^{I} ions through a common O atom. This type of coordination provides the binding of two {CoLi(L)(Piv)$_3$} moieties by two Li–O bonds. The tetranuclear fragment {CoLiLiCo} forms a zigzag chain in which all atoms lie in the same plane. The bond lengths and angles in molecules **1** and **2** are within the typical range for each bond type.†

Based on the analysis carried out in the SHAPE 2.1 program,[29] the coordination environment of Co ions (CoO_3C in complex **1** and CoO_3P in complex **2**) can be described as pseudo-tetrahedral {**1**: S_Q[Co(1)] = 0.805, S_Q[Co(2)] = 0.831, S_Q[Co(3)] = 0.421, S_Q[Co(4)] = 1.355; **2**: S_Q[Co(1)] = 1.154}. Li ions are in a strongly distorted tetrahedral environment formed by four O atoms of carboxyl groups.

The coordination of bulky ancillary ligands with Co atoms does not significantly affect the structure of the resulting complexes, and the coordination geometry of the {Co_2Li_2} tetranuclear fragment in complexes **1** and **2** is similar to that in the previously reported compounds with pyridine,[25] 2,4-lutidine[26] and Et_3N.[30] The crystal packing of compound **1** is stabilized due to the CH···π interactions,† whereas in the crystal structure of compound **2**, no significantly shortened intermolecular interactions were found.

The magnetic behaviour of complexes **1**, **2** and **5** was investigated under an applied dc magnetic field of 5000 Oe in the temperature range of 2–300 K. The temperature dependence of the molar magnetic susceptibility $\chi_M T(T)$ for compounds **1**, **2** and **5** (Figure 3) looks typical for mononuclear complexes of Co^{2+} ions with pseudo-tetrahedral coordination. The $\chi_M T$ values at 300 K (5.16, 5.13 and 5.09 cm^3 K mol^{-1} for complexes **1**, **2** and **5**, respectively) are much higher than the spin-only value for two magnetically isolated Co^{2+} ions (3.744 cm^3 K mol^{-1}), which indicates the contribution of the orbital magnetic momentum. On cooling, the $\chi_M T$ values gradually decrease and at 2 K reach the minimum magnitudes of 2.74, 2.94 and 2.64 cm^3 K mol^{-1} for complexes **1**, **2** and **5**, respectively. This behaviour is most likely associated with the anisotropy of Co^{2+} ions and the Zeeman (saturation) effect induced by a dc magnetic field.[31–33]

To estimate the parameters of local magnetic anisotropy in complexes **1**, **2** and **5**, we approximated† the $\chi_M T(T)$ dependences using the PHI program[34] (Table 1 and Figure 3) with the effective spin Hamiltonian:

$$\hat{H} = D\hat{S}_z^2 + g_{iso}\mu_B SB, \quad (1)$$

where the first term represents the axial zero-field splitting, and the second is the Zeeman contribution. Strong correlations were found between the refined parameters in an attempt to simultaneously evaluate the three projections of *g*-factor and *D*. For this reason, isotropic *g*-factors, together with *D*, were used as approximation parameters. From the shape of the high-temperature sections of the graphs, one can deduce a significant contribution of temperature-independent paramagnetism (TIP), which was taken into account in the approximation. Several works have already

‡ *Crystal data for* **1**. $C_{144}H_{204}Co_4Li_4N_8O_{24}$ (M = 2694.62), T = 293 K, triclinic, space group $P\bar{1}$, a = 14.770(7), b = 23.750(9) and c = 23.868(9) Å, α = 91.855(10)°, β = 91.182(18)°, γ = 100.503(18)°, V = 8225(6) Å^3, Z = 2, μ(MoKα) = 0.456 mm^{-1}. At the angles 1.946° < 2θ < 23.256°, 59641 reflections were measured, including 23601 unique reflections (R_{int} = 0.1933) and 8179 reflections with $I > 2\sigma(I)$, which were used in the calculations. The final R_1 = 0.2887, wR_2 = 0.3505 (all data) and R_1 = 0.1176, wR_2 = 0.2578 [$I > 2\sigma(I)$], GOOF = 0.987, largest diff. peak/hole 0.920/–0.606 eÅ^{-3}.

Crystal data for **2**. $C_{66}H_{84}Co_2Li_2O_{12}P_2$ (M = 1263.01), T = 296 K, triclinic, space group $P\bar{1}$, a = 10.897(5), b = 12.835(5) and c = 14.426(8) Å, α = 93.188(16)°, β = 110.959(11)°, γ = 105.603(11)°, V = 1788.6(15) Å^3, Z = 1, μ(MoKα) = 0.562 mm^{-1}. At the angles 2.400° < 2θ < 25.998°, 12264 reflections were measured, including 6772 unique reflections (R_{int} = 0.0974) and 2178 reflections with $I > 2\sigma(I)$, which were used in the calculations. The final R_1 = 0.2456, wR_2 = 0.3173 (all data) and R_1 = 0.0956, wR_2 = 0.2358 [$I > 2\sigma(I)$], GOOF = 0.898, largest diff. peak/hole 0.592/–0.829 eÅ^{-3}.

Crystal data for **5**. $C_{40}H_{28}Co_2Li_2N_2O_{18}$ (M = 956.38), T = 296 K, triclinic, space group $P\bar{1}$, a = 10.1897(13), b = 10.3386(15) and c = 10.9695(16) Å, α = 96.769(5)°, β = 94.581(6)°, γ = 116.338(4)°, V = 1017.0(2) Å^3, Z = 1, μ(MoKα) = 0.897 mm^{-1}. At the angles 2.231° < 2θ < 26.364°, 9815 reflections were measured, including 4145 unique reflections (R_{int} = 0.0769) and 2525 reflections with $I > 2\sigma(I)$, which were used in the calculations. The final R_1 = 0.1397, wR_2 = 0.2351 (all data) and R_1 = 0.0865, wR_2 = 0.2018 [$I > 2\sigma(I)$], GOOF = 1.121, largest diff. peak/hole 0.814/–0.840 eÅ^{-3}.

The XRD analysis was accomplished on a Bruker APEX-II diffractometer using a standard procedure (MoKα irradiation, graphite monochromator, λ = 0.71073 Å, ω-scans with 1° step). Using Olex2,[27] the structure was solved with the SHELXS structure solution program using direct methods and refined using the SHELXL[28] refinement package with the least-squares minimization in an anisotropic approximation for nonhydrogen atoms. The H atoms were added in the calculated positions and refined using the riding model in an isotropic approximation. The polyhedron geometry of metals was calculated using the SHAPE 2.1 software.[29]

CCDC 2061650, 2061653 and 2069120 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 1 The parameters of approximation of the $\chi_M T(T)$ dependences for complexes **1**, **2**, **4** and **5**, obtained using the PHI program, and the parameters of the quantum-chemical calculation (QCC) of D and the g tensor for complexes **1**–**5**.

Complex	Method	Fitting parameter					
		g_x	g_y	g_z	g_{iso}	D/cm^{-1}	E/D
1	PHI	–	–	–	2.207	10.4	–
	QCC[a]	2.304	2.232	2.134	2.223	15.02	0.218
2	PHI	–	–	–	2.274	20.5	–
	QCC	2.344	2.255	2.044	2.214	28.82	0.138
3	QCC	2.431	2.274	2.082	2.262	28.45	0.248
4	PHI	–	–	–	2.232	13.2	–
	QCC	2.415	2.246	2.108	2.256	23.85	0.332
5	PHI	–	–	–	2.257	18	–
	QCC	2.32	2.27	2.09	2.227	22.69	0.097

[a] Average values over four crystallographically nonequivalent Co^{II} ions in structure **1**.†

mentioned the importance of the TIP contribution for tetrahedral Co^{II} complexes.[35,36] The best-fitting values of the parameters† are presented in Table 1.

To elucidate the effect of the nature of the auxiliary ligand L on the magnetic characteristics of the Co^{2+} ion in the $\{CoO_3X\}$ pseudo-tetrahedral environment, we analyzed the data for the known Li_2Co_2 complexes with N-donor ligands. Three complexes with a similar geometry of the metal carboxylate core, namely $[Co_2Li_2(Piv)_6(py)_2]$ **3**,[25] $[Co_2Li_2(Piv)_6(lut)_2]$ **4**[26] and $[Co_2Li_2(Fur)_6(py)_2]$ **5**† were chosen. The parameters of the best approximation of the $\chi_M T(T)$ dependences for complexes **4** and **5** (Table 1) were obtained by the PHI program using the same effective spin Hamiltonian equation (1).†

The calculated values of D and g_{iso} (Table 1) are in good agreement with the experimental ones for all complexes. It should be noted that various structural distortions in the coordination environment of Co^{II} ions, which are observed in complex **1**, do not significantly affect the calculated parameter of magnetic anisotropy. For various nonequivalent Co^{II} ions, parameter D, as well as the components of the g-tensor, remain in a narrow range (Table 1).† On the other hand, even small changes in the nature of the N-heterocyclic ligand can significantly affect the local magnetic anisotropy of the Co^{II} ion.[37] This statement is evidenced by a comparative examination of the calculated data for complexes **3**–**5**. Moreover, a significant, almost two-fold increase in the magnetic anisotropy is observed on going from the N-heterocyclic carbene IMes to the triphenylphosphine ligand. This enhancement of properties is additionally facilitated by the local C_{3v} symmetry of the Co^{II} ion coordination environment since pseudo-tetrahedral Co^{II} complexes with two carbene[35] or

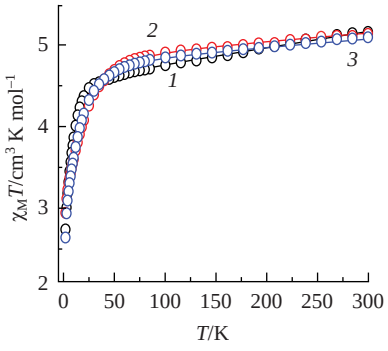


Figure 3 Temperature dependence of the molar magnetic susceptibility $\chi_M T$ for complexes (*1*) **1**, (*2*) **2** and (*3*) **5** under an applied dc magnetic field of 5000 Oe. Solid lines represent the theoretical curves.

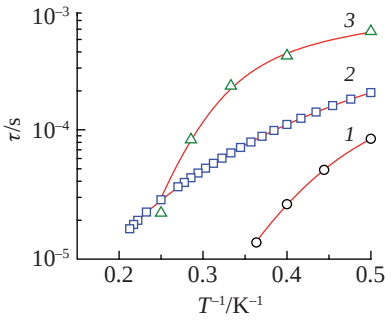


Figure 4 The dependence of the magnetization relaxation time τ on the reciprocal temperature T^{-1} for complexes (*1*) **1**, (*2*) **2** and (*3*) **5** under an optimal dc magnetic field of 2500, 1000 and 1000 Oe, respectively. Solid lines represent fitting by the sum of the Raman and direct relaxation mechanisms.

two triphenylphosphine ligands[23] have the C_{2v} symmetry and show much lower values of the parameter D.

It is known that mono- and polynuclear Co^{II} complexes often exhibit SMM behaviour. We investigated the magnetic behaviour of the compounds obtained in an alternating magnetic field to test whether they exhibit slow magnetic relaxation. Dynamic magnetic behaviour was investigated both in zero dc magnetic field and in magnetic fields up to 5000 Oe.†

In the zero dc magnetic field, slow magnetization relaxation was not observed for complexes **1**, **2** and **5**. However, under applied fields, significant out-of-phase signals for all three complexes appeared at optimal dc fields: 2500 Oe for **1** and 1000 Oe for **2** and **5**. This behaviour possibly originates from suppressing quantum tunnelling mechanism (QTM), which can drastically accelerate magnetic relaxation.† Frequency dependences of the in-phase and out-of-phase components of the ac magnetic susceptibility were measured for complexes **1**, **2** and **5** under optimal H_{dc} fields.†

The approximation of the χ'' frequency dependences measured at different temperatures using the generalized Debye model led to the temperature dependences of the relaxation time $\tau(T^{-1})$, shown in Figure 4. The overall nonlinear shape of the $\tau(T^{-1})$ curves suggests that non-Orbach mechanisms are involved in magnetization relaxation.

According to quantum chemical calculations, the value of the zero-field splitting parameter D for complexes **1**, **2** and **5** is greater than zero, which means that the Orbach relaxation mechanism is impossible. Based on this conclusion, all possible combinations of the Raman, direct and QTM relaxation mechanisms were used to search for the best approximation for $\tau(T^{-1})$.

For complexes **1**, **2** and **5**, the temperature dependence of the relaxation time is most accurately described by equation (2) that summarizes the Raman and direct relaxation mechanisms:

$$\tau^{-1} = C_{Raman} T^{n_{Raman}} + A_{direct} T H^4, \quad (2)$$

with the following parameter values: 19 (±6), 326 (±8) and 0.12 (±0.01) s^{-1} K$^{-n_{Raman}}$ for C_{Raman}, 8.0 (±0.4), 3.29 (±0.02) and 9 (fixed) for n_{Raman}, and 8.8×10^{-11} ($\pm 6 \times 10^{-12}$), 9.8×10^{-10} ($\pm 2 \times 10^{-11}$) and 8.5×10^{-10} ($\pm 2 \times 10^{-11}$) K^{-1} Oe^{-4} s^{-1} for A_{direct}, respectively.

Thus, we have shown that a change in the nature of the carboxylate and ancillary donor ligands does not make a significant impact on the structure of the tetranuclear $\{Co_2Li_2\}$ complexes but can affect the electronic characteristics of Co^{II} ions in such complexes. *Ab initio* SA-CASSCF/NEVPT2 calculations revealed that replacement of ancillary donor ligands in the $\{CoO_3X\}$ tetrahedron (X = N, P and C) from pyridine to Ph_3P and NHC allows tuning the magnetic anisotropy parameter D due to the enrichment of the electronic density from the σ-donor. The results of quantum-chemical calculations agree with the approximation of the experimental dependences of $\chi_M T$ on T. The field-induced slow magnetic relaxation in compounds **1**, **2** and **5** was detected

from the measurements in the ac magnetic field. It is described by the sum of the Raman and direct mechanisms.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.011.

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