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Syntheses and Structures of Three Complexes of Formulas $[L_3Co(\mu_2\text{-}O_2P(Bn)_2)_3CoL'][L'']$, Featuring Octahedral and Tetrahedral Cobalt(II) Geometries; Variable-Temperature Magnetic Susceptibility Measurement and Analysis on $[(py)_3Co(\mu_2\text{-}O_2PBn_2)_3Co(py)][ClO_4]$

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Supporting Information

ABSTRACT: The syntheses and structural properties of three dinuclear complexes $[L_3Co(\mu_2\text{-}O_2P(Bn)_2)_3CoL'][L'']$ [one ionic L_3 = py$_3$, L′ = py, L″ = ClO_4^- (**1**) and two molecular L_3 = py$_3$, L′ = Cl (**2**) and L_3 = py, μ_2-NO_3^-, L′ = py (**3**)] are reported. Complexes feature octahedral Co^{II} sites bridged by three dibenzylphosphinate ligands to a tetrahedrally ligated Co^{II} site, with the remaining coordination sites occupied by py, nitrato, and Cl ligands. The Co−Co distances are 4.248 Å at 291 K and 4.265 Å at 100 K for **1** and 4.278 and 4.0313(7) Å for **2** and **3**, respectively at 100 K. A fit of the low-temperature magnetic susceptibility data was derived for complex **1** with $g = 2.25$, TIP = 700×10^{-6} cm^3 mol^{-1}, $\lambda = -173$ cm^{-1}, $\kappa = 0.93$, $\nu = -3.9$, $\Delta = 630$ cm^{-1}, $J = 0.15$ cm^{-1}, and $\theta = -1.8$ resulting in $R(\chi_M) = 2.5 \times 10^{-5}$ and $R(\chi_M T) = 5.8 \times 10^{-5}$.

Dinuclear cobalt complexes featuring octahedral and tetrahedral geometries with Co^{III}−Co^{II}[1,2] and Co^{II}−Co^{II}[3−5] centers have been reported. Magnetic studies have been reported for three of the Co^{II}−Co^{II} compounds, which have very different bridging ligands. First, for compound $[(H_2O)(dppm)_2Co(\mu\text{-}CN)CoCl_3]$, high-spin isolation ($S = {}^3/_2$) pertained, but the linear nature of the data obtained (i.e., $\chi_M T$ vs T was linear) could not be satisfactorily analyzed.[3] Second, for complex $[Co_2L_2Cl_3]Cl$, L = 2,6-diamino-3-[(2-carboxymethyl)phenylazo]pyridine, analysis of the magnetic data resulted in the conclusion that "two low-spin Co^{2+} ions pertained."[4] Third, for compound $[(MeCN)_5Co(NCS)Co(NCS)_3]$ (**4**), magnetic analysis suggested that the data can be best fit with the Curie−Weiss expression with $g_{avg} = 2.5$ and $\theta = -15.5$ K.[5] The Co−Co distances in these compounds were 5.007, 4.800, and 5.732 Å for the first to third, respectively.

Our interest in the complexes reported herein stems from our discovery that the dibenzylphosphinate ligand stabilizes tetrameric clusters such as $[V_4O_8]^{4+}$, $[Mo_4O_8]^{4+}$, and $[W_4O_8]^{4+}$.[6−9] Previous research reacting phosphinate ligands and cobalt have resulted in polymeric species.[10−17] In an extension of this work to prepare clusters of cobalt(III) oxides or hydroxides,[18] we find that this ligand affords dinuclear clusters of the form $[L_3Co(\mu_2\text{-}O_2P(CH_2C_6H_5)_2)_3CoL'][L'']$. Dark-blue crystals of $[(py)_3Co(\mu_2\text{-}O_2PBn_2)_3Co(py)][ClO_4]$ (**1**) were isolated first from an ethanol solution consisting of a mixture of Bn_2PO_2K, $Co(ClO_4)_2{\cdot}6H_2O$, pyridine (py), and H_2O_2.[19] It was later discovered that **1** can be made in good yield by reacting 3 equiv of the potassium salt of the ligand with 2 equiv of cobalt perchlorate along with excess py in ethanol. Compound $[(py)_3Co(\mu_2\text{-}O_2P(Bn_2)_3Co(Cl)]$ (**2**) was also first prepared unintentionally from the reaction of $Co(NO_3)_2{\cdot}6H_2O$ with py and Bn_2PO_2H in dichloromethane (DCM). The addition of hexanes resulted in the formation of light-pink crystals, which were found to be the known compound $Co(NO_3)_2(H_2O)_2(py)_2$. The solution was filtered, and the addition of more hexanes produced dark-blue crystals of **2**. The chloride ion may have been produced from the reaction of py with DCM,[20] and we have discovered that compound **2** can be produced starting with $CoCl_2{\cdot}6H_2O$. Complex $[(py)(\mu_2\text{-}NO_3)Co(\mu_2\text{-}O_2PBn_2)_3Co(py)]$ (**3**) was obtained serendipitously in a reaction of $Co^{III}(acac)_2PyNO_2$ and Bn_2PO_2H under reflux conditions in $CHCl_3$. The addition of pentane, followed by keeping the solution at 5 °C for 2 weeks, leads to the formation of dark-purple crystals of **3**.

A thermal ellipsoid plot of **1** is illustrated in Figure 1. In all structures, the two Co centers are bridged by three dibenzylphosphinate ligands. This ligand is very flexible and is capable of bridging at various lengths, as illustrated in the Co−Co distances in these compounds, which are 4.265(2), 4.278(1), and 4.0313(7) Å for **1**−**3**, respectively. Complexes **1** and **2** were arranged with the octahedrally coordinated Co atom arranged on a 3-fold axis and the tetrahedrally coordinated Co atom located slightly off the 3-fold axis. In **1**, three py ligands complete the octahedral geometry at one end and the other end has one py coordinated. The complex is

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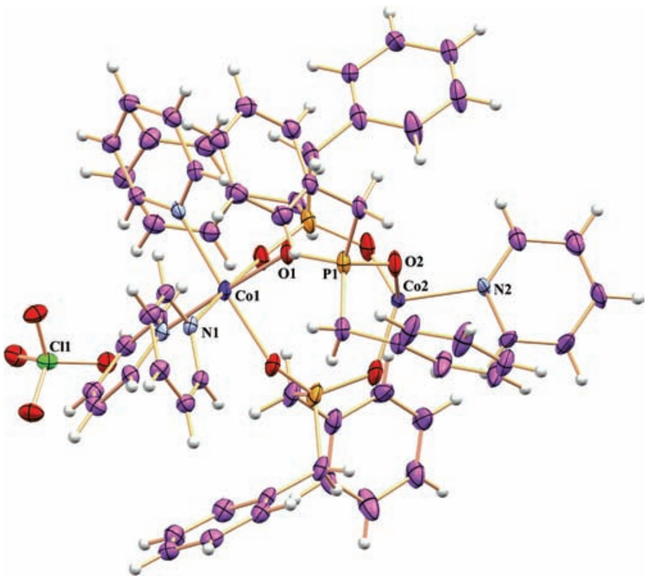

Figure 1. Thermal ellipsoid drawing of **1**-100K (one orientation). Selected bond distances (Å) and angles (deg) are as follows: Co1−O1, 2.103(2); Co1−N1, 2.192(2); Co2−O2, 1.813(17); Co2−N2, 2.045(4); O1^a−Co1−O1, 91.18(8); O1^a−Co1−N1, 86.86(9); O1^b−Co1−N1, 177.33(8); O1−Co1−N1, 87.04(8); N1−Co1−N1^a, 94.85(7); O2−Co2−O2^b, 125.65(13); O2−Co2−N2, 103.6(7); O2−Co2−O2^a, 106.3(7); O2^b−Co2−O2^a, 106.0(6); O2^b−Co2−N2, 111.3(8); N2−Co2−O2^a, 101.6(2). Symmetry transformation codes: a, −*y*, *x* − *y*, *z*; b, −*x* + *y*, −*x*, *z*.

positively charged and is balanced by a $[ClO_4]^-$ anion, as illustrated in Figure 1.

Compound **2** has a similar octahedral geometry with three py ligands, but at the other site, one chloride ligand completes the tetrahedral arrangement. This complex also has the Co atoms and the Cl ligand situated on a 3-fold axis, but both benzyl groups are disordered. Compound **3** has a nitrato ligand coordinated in a bidentate manner together with one py ligand at the octahedral Co site and one py ligand at the other. Ring strain in the four-membered ring of the nitrato ligand is responsible for the longer Co−O distances at Co2−O7, 2.188(3) Å, and Co2−O8, 2.211(3) Å, compared to the other Co−O distances at the octahedral site in **3**, which range from 2.031(2) to 2.069(2) Å.[21] This complex did contain the shortest Co−Co distance at 4.0313(7) Å within compounds **1**−**3**, and all feature octahedral and tetrahedral Co centers. The bridging phosphinate ligands are asymmetrically bonded in that the Co−O distances are significantly longer at the octahedral site in comparison to those at the tetrahedral end, i.e., 2.103(2) and 2.102(4) Å compared to 1.813(17) and 1.973(5) Å for **1** and **2**, respectively. The disorder in these molecules hindered a more accurate determination, but for **3**, the distances at 2.031(2), 2.032(3), and 2.069(2) Å at the octahedral end were also significantly longer than those at the tetrahedral site at 1.955(2), 1.933(2), and 1.940(2) Å for Co−O bonds on phosphinate ligands P1, P2, and P3, respectively, all presumably because of steric reasons.

The $\chi_M T$ data for **1** and **2** were determined at room temperature (ca. 290 K) using a Johnson Matthey Gouy balance to be 5.56 and 6.59 emu K mol^{-1}, respectively. These values are larger than the spin-only value for two high-spin Co^{II} sites (3.75 emu K mol^{-1}) and suggests that there is a contribution of orbital angular momentum typical of the local $^4T_1$ term.[22] The temperature-dependent data χ_M on **1** were obtained using a SQUID magnetometer over the temperature range 2.0−300 K under a 1000 Oe measuring field, and this is illustrated in Figure 2, together with the $\chi_M T$ dependence. At 300 K, the $\chi_M T$ value for **1** was 5.813 emu K mol^{-1} compared to 5.575 emu K mol^{-1} reported for **4**.[5] As shown in Figure 2, $\chi_M T$ versus *T* for **1** decreases slowly from 5.813 emu K mol^{-1} at 300 K to 4.575 emu K mol^{-1} at 50 K and then more rapidly to 2.254 emu K mol^{-1} at 2 K. We were unable to determine a satisfactory fit to the data using the Curie−Weiss equation, but this is not surprising because analysis of high-spin cobalt(II) complexes is known to be difficult.[23−30]

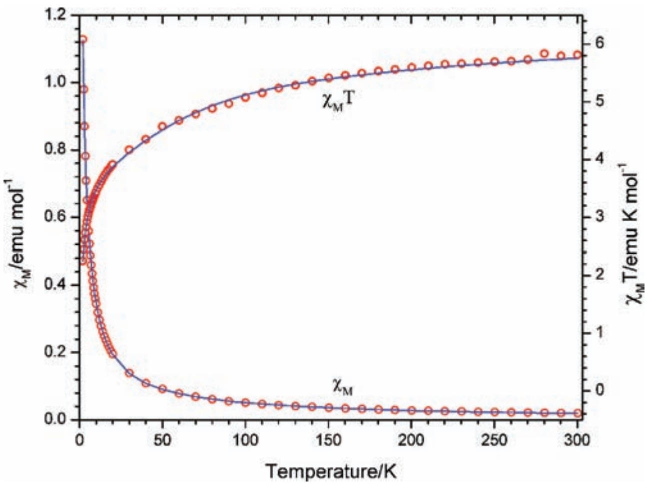

Figure 2. Temperature dependence of χ_M vs *T* and $\chi_M T$ vs *T* for **1** with data represented by open circles and the solid-line fit obtained using the parameters described in the text.

A fit of the data for **1** and **4** was calculated using the equations presented as Supporting Information; see Table 1. This analysis involved consideration of the *g* factor and temperature-independent paramagnetism (TIP) for the tetrahedral Co^{II} ion, the spin−orbit coupling factor λ, the orbital reduction factor κ, and a distortion parameter ν defined as $\Delta/\kappa\lambda$ for the octahedral Co^{II} ion, and the intramolecular exchange interaction *J* and the Weiss constant θ to describe the intermolecular exchange interaction. In general, it is difficult to separate the intramolecular interaction from the intermolecular interaction. In particular, when *J* is negative, it is almost impossible to determine *J* and θ correctly. If the calculation for the fit of the low-temperature data modified *J* without consideration of θ, the quality of the fit was not good; however, this improved when θ was used instead of *J*. Interestingly, when *J* and θ were simultaneously optimized, *J* became positive (but small at 0.15 cm^{-1}) and the lowest R_χ value (i.e., even higher fitting quality) was obtained. The value for the spin−orbit parameter λ of −173 cm^{-1} for **1** is noteworthy for the theoretical value for the free Co^{II} ion is expected to be ~−172 cm^{-1}.[31] That for κ at 0.93 is also close to that for the free Co^{II} ion.[32] Both of these parameters were calculated to be slightly less in complex **4**.[5] The values for Δ at 630 and 510 cm^{-1} for **1** and **4**, respectively, are normal for octahedral high-spin cobalt(II) complexes (~200 to ~800 cm^{-1}).[33] For **1**, the negative ν value of −3.9 and the Δ value of 630 cm^{-1} suggest that the octahedral Co^{II} ion is trigonally compressed, and this is also consistent with the crystal structure of **1**, where O1^a−Co1−O1 and N1−Co1−N1^a are larger than

Table 1. Magnetic Parameters[a]

complex	g	TIP, emu mol^{-1}	λ, cm^{-1}	κ	ν	Δ, cm^{-1}	J, cm^{-1}	θ, K	R_{χ},[b] $\times 10^{-5}$	$R_{\chi T}$,[c] $\times 10^{-5}$
1	2.25	0.0007	−173	0.93	−3.9	630	0.15	−1.8	2.5	5.8
4[d]	2.17	0.0007	−155	0.89	−3.7	510	−2.62	−0.1	15	16

[a] Calculated as in the Supporting Information. [b] $R_{\chi} = \sum(\chi_{M,calc} - \chi_{M,obs})^2/\sum(\chi_{M,obs})^2$. [c] $R_{\chi T} = \sum(\chi_{M,calc}T - \chi_{M,obs}T)^2/\sum(\chi_{M,obs}T)^2$. [d] L = MeCN, L′ = NCS.[5]

90° and O1^a−Co1−N1 and O1−Co1−N1 are smaller than 90°.[34] In conclusion, for complex **4**,[5] if J is assumed to be 0, $|\theta|$ becomes large and unreasonable. Therefore, the sign and magnitude of the J value at −2.62 cm^{-1} in Table 1 are suggestive of antiferromagnetic interactions. However, in the case of **1**, the magnitude of J at 0.15 cm^{-1} is small and indicative of very weak exchange interactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparations, FTIR spectra, equations for magnetic analysis, and CIF files for **1**-291K, **1**-100K, **2**-100K, and **3**-100K (CCDC 869796−869799). This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for these structures have also been deposited with the Cambridge Crystallographic Data Centre. They can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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Notes

The authors declare no competing financial interest.

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(19) Crystal data for **1**: $C_{62}H_{62}Co_2N_4O_6P_3 \cdot ClO_4$, M = 1269.38, hexagonal, $a = b$ = 13.5260(10) Å, c = 57.341(4) Å, V = 9085.2(11) Å^3, T = 100(2) K, space group $R\bar{3}$, Z = 6, 14927 reflections measured, 5028 independent reflections (R_{int} = 0.0311). R1 = 0.0518 [$I > 2\sigma(I)$] and wR2(F^2) = 0.1126 [$I > 2\sigma(I)$]. GOF on F^2 =1.018.

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