

Coordination properties of the diethyl 2-pyridylmethylphosphonate ligand (2-pmpe) with chloride transition-metal salts: X-ray crystal structure of $\text{Cd}_4(2\text{-pmpe})_4\text{Cl}_8$

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Abstract

A new series of the chloride transition-metal complexes containing the ligand diethyl 2-pyridylmethylphosphonate (2-pmpe) of general formula $\text{M}(2\text{-pmpe})_2\text{Cl}_2$ ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}$) and $\text{M}(2\text{-pmpe})\text{Cl}_2$ ($\text{M} = \text{Co}, \text{Zn}$) were prepared. The complexes were identified and characterized by elemental analysis, spectroscopic and magnetic studies. For $\text{Cd}_4(2\text{-pmpe})_4\text{Cl}_8$ X-ray crystal structure was determined. The structure is based on a chloro-bridged tetranuclearcadmium quasi cubane cluster, in which each cadmium atom is chelated by one N,O-chelate 2-pmpe ligand and coordinated with four bridging chloride atoms. The ligand containing two donor atoms, heterocyclic pyridyl nitrogen and phosphoryl oxygen atoms binds in a didentate chelate manner in all complexes. Two compounds were obtained with cobalt chloride salt, exhibiting tetrahedral (1:1) and octahedral (1:2 metal to ligand molar ratio) arrangements of cobalt ions. The octahedral Ni(II), Co(II) and Mn(II) complexes are isostructural. Geometry of $\text{Zn}(2\text{-pmpe})\text{Cl}_2$ is consistent with a pseudotetrahedral environment of Zn(II) ion. The spectroscopic properties of Zn(II), and magnetic behavior of Ni(II), Co(II) and Mn(II) complexes indicate mononuclear structure of all compounds.

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1. Introduction

Complexes of transition metals with phosphonate ligands containing mononitrogen aromatic bases such as pyridine and quinoline are of considerable interest because of their interesting structures, reactivity and biological and catalytic activity.

In previous study, the results of spectroscopic and magnetic studies on transition-metal complexes with the substituted pyridine and quinoline e.g. the diethyl 2-pyridyl-, 4-pyridyl- and 2-quinolylmethylphosphonate ligands [1] (2-pmpe, 4-pmpe and 2-qmpe, respectively), containing two potential donor atoms, the heterocyclic nitrogen and

phosphoryl oxygen atoms, were reported [2–6]. Scheme drawing of 2-pmpe ligand is shown in Fig. 1. Crystal structure of the representative compounds i.e. $[\text{Co}(4\text{-pmpe})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (with N,O-bridging ligand) [2], $\text{Co}(2\text{-pmpe})_2\text{Cl}_2$ (with N,O-chelate ligand) [6] and $[\text{M}(2\text{-qmpe})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (with O-bonded ligand), where $\text{M} = \text{Ni}, \text{Mn}$ [3] were determined.

It is worth to note that the interaction of 2-pmpe and 2-qmpe with some copper(II) salts leads to oxidative P-dealkylation/dephosphorylation of the 2-pmpe and 2-qmpe ligands [5]. In this framework, we are interested in the preparation and examine the coordination behavior of 2-pmpe ligand with chloride transition-metal salts. The compounds and their possible structure are discussed on the basis of the spectral and magnetic studies. For cadmium compound crystal data are discussed.

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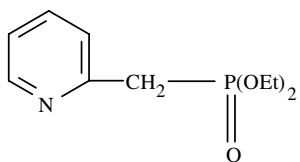


Fig. 1. A schematic drawing of the 2-pmpe ligand.

2. Experimental

2.1. Reagents and physical measurements

The starting materials and solvents for synthesis were obtained commercially and used as received. Metal content was determined using a Carl Zeiss Jena atomic absorption spectrophotometer and a ARL Model 3410 ICP spectrometer. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer 2400CHN. Solid-state electronic spectra (28,000–4000 cm^{-1}) were performed on a Cary 500 spectrophotometer. Solid-state EPR spectra were recorded at room temperature, at 77 K on a Bruker ESP 300E spectrometer operating at X-band, equipped with a Bruker NMR gaussmeter ER 0.35 M and a Hewlett Packard microwave frequency counter HP 5350B.

Magnetic measurements were carried out on solid polycrystalline samples with a Faraday method in the temperature range 77–300 K by using a sensitive Sartorius M-25D electrobalance. The susceptometer was equipped with an Oxford Instruments CF-1200 continuous-flow cryostat and an electromagnet operating at 5.25 kG. The calibrant employed was $\text{HgCo}(\text{NCS})_4$ for which the susceptibility was assumed to be $16.44 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ [7]. The corrections for diamagnetism of the constituent atoms were made by use of Pascal constants [8] and the effective magnetic moments were calculated from $\mu_{\text{eff}} = 2.83(\chi_{\text{M}}T)^{1/2}$ using temperature-independent paramagnetism (TIP) of $244 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Ni (1), $150 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Co (2) and $576 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for Co (3) [8–10].

2.2. X-ray crystallography

X-ray data were collected at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ -axis diffractometer with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal was positioned at 65 mm from the CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 20 s. Accurate cell parameters were determined and refined by least-squares fit of 5100 the strongest reflections. The data were corrected for Lorentz and polarization effects. An analytical absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction (Poland). The structure was solved by direct methods (program SHELXS97 [11]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 [12] programs. Non-hydrogen atoms

Table 1

Crystal data and structure refinement for $\text{Cd}_4(2\text{-pmpe})_4\text{Cl}_8$

| | |
|--|---|
| Empirical formula | $\text{C}_{40}\text{H}_{64}\text{N}_4\text{O}_{12}\text{Cl}_8\text{P}_4\text{Cd}_4$ |
| Formula weight | 1650.04 |
| T/K | 100(2) |
| $\lambda/\text{\AA}$ | 0.71073 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a/\text{\AA}$ | 9.128(2) |
| $b/\text{\AA}$ | 12.468(2) |
| $c/\text{\AA}$ | 15.082(3) |
| $\alpha/^\circ$ | 66.29(1) |
| $\beta/^\circ$ | 79.06(1) |
| $\gamma/^\circ$ | 77.58(1) |
| $V/\text{\AA}^3$ | 1524.66(15) |
| Z | 1 |
| $D_c/\text{Mg m}^{-3}$ | 1.797 |
| μ/mm^{-1} | 1.886 |
| $F(000)$ | 816 |
| Crystal size/mm | $0.20 \times 0.17 \times 0.15$ |
| θ range for data collection/ $^\circ$ | 2.97–27.50 |
| Ranges of h, k, l | $-10 \rightarrow 11, -16 \rightarrow 16, -19 \rightarrow 19$ |
| Reflections collected | 17670 |
| Independent reflections (R_{int}) | 6870(0.0546) |
| Data/parameters | 6870/379 |
| Absorption coefficients min/max | 0.704/0.765 |
| GOF(F^2) | 0.975 |
| Final R_1/wR_2 indices ($I > 2\sigma_I$) | 0.0397/0.0729 |
| Largest diff. peak/hole / $e \text{ \AA}^{-3}$ | 0.634/−0.608 |

were refined with anisotropic displacement parameters; hydrogen atoms were included from geometry of molecules and $\Delta\rho$ maps. They were treated as rigid group during refinement. Crystal data are given in Table 1, together with refinement details.

2.3. Synthesis of the ligand and complexes

Ligand the diethyl 2-pyridylmethylphosphonate (2-pmpe) was prepared according to the procedure described in detail elsewhere [2].

The chloride complexes were prepared by dissolving the appropriate hydrated metal chloride (1 mmol) in ethanol (10 cm^3) and adding to a solution of the ligand (1 or 2 mmol) in ethanol (20 cm^3). After filtration of the hot reaction mixture, to remove any impurities, the complexes crystallized on cooling. In some case, however, evaporation of part of the solvent was necessary before crystallization would occur.

The chloride complexes 1:1 and 1:2 were prepared as described above using metal chloride hexahydrate and 2-pmpe ligand (1 mmol) and (2 mmol), respectively.

Anal. Found: C, 40.75; H, 5.51; N, 4.57; Ni, 10.15; Calcd for $[\text{C}_{20}\text{H}_{32}\text{N}_2\text{P}_2\text{O}_6\text{Cl}_2\text{Ni}]$ (1): C, 40.84; H, 5.49; N, 4.76; Ni, 9.98%.

Anal. Found: C, 41.22; H, 5.62; N, 4.89; Co, 10.53; Calcd for $[\text{C}_{20}\text{H}_{32}\text{N}_2\text{P}_2\text{O}_6\text{Cl}_2\text{Co}]$ (2): C, 40.82; H, 5.49; N, 4.76; Co, 10.02%.

Anal. Found: C, 33.77; H, 4.18; N, 3.59; Co, 16.80; Calcd for $[\text{C}_{10}\text{H}_{16}\text{NPO}_3\text{Cl}_2\text{Co}]$ (3): C, 33.44; H, 4.50; N, 3.90; Co, 16.41%.

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