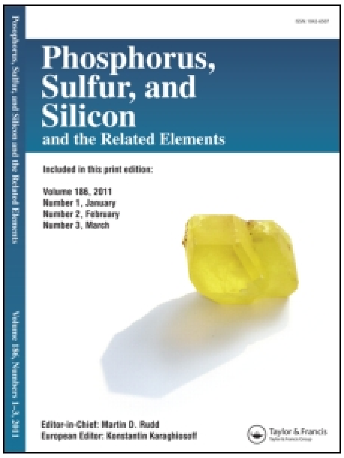

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TRANSITION METAL COMPLEXES OF DIETHYL-(2-OXO-1-PHENYLETHYL)PHOSPHONATE

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TRANSITION METAL COMPLEXES OF DIETHYL-(2-OXO-1-PHENYLETHYL)PHOSPHONATE

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The cobalt(II)-, nickel(II)- and copper(II)-complexes of diethyl-(2-oxo-1-phenylethyl)phosphonate **1** (**2**, **3**, and **4**, respectively) are synthesized using the corresponding metal acetates. Their structure is studied by spectroscopic (IR, electronic and EPR) and magnetochemical methods. The experimental data indicate that the cobalt and nickel complexes **2** and **3** are octahedrically coordinated by the bidentate phosphonyl and acetate ligands. EPR evidences of the formation of two different Cu(II) complex species in solution are also obtained.

Key words: Diethyl-(2-oxo-1-phenylethyl)phosphonate, cobalt(II) complex; nickel(II) complex; copper(II) complex.

INTRODUCTION

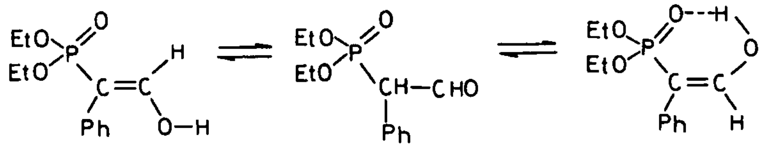
In previous papers[1,2] we have studied the reactivity of esters of 2-oxo-alkyl and 2-oxo-phenylalkyl phosphonic acids in reactions of salt and complex formation. It was shown that the lithium salt of diethyl-(1-methyl-2-oxoethyl)phosphonate exists as a mixture of (*Z*)- and (*E*)-forms, while the lithium salt and zinc complex of diethyl-(2-oxo-1-phenylethyl)phosphonate **1** have (*Z*)-chelate structure.

In the present paper we report the synthesis and characterization of cobalt(II)-, nickel(II)- and copper(II)-complexes of diethyl-(2-oxo-1-phenylethyl)-phosphonate **1** (**2**, **3** and **4**, respectively).

RESULTS AND DISCUSSION

The ligand **1** was obtained according to Reference 3, using ethyl formate as formylating agent. It was a mixture of aldehyde **1a**, (*Z*)- and (*E*)-enol forms (**1b** and **1c**) which indicates that, unlike β-dicarbonyl compounds, (*E*)-tautomer appear to have similar stabilization by intermolecular H-bonding as the intramolecular bonding in the (*Z*)-tautomer.[2]

The Co(II) complex **2** and Ni(II) complex **3** of the ligand **1** were obtained using



1c 1a 1b

FIGURE 1 Aldo-enol tautomerism of diethyl-(2-oxo-1-phenylethyl)phosphonate.

the corresponding acetates (metal to ligand ratio 1:2) in methanol at room temperature. The composition of the complexes was proven by elemental analysis and their structure were studied by means of spectroscopic (IR, electronic and EPR) and magnetochemical methods. The elemental analysis data showed metal to ligand to acetate ratio of 1:1:1. The IR spectral data are given in Table I. The complexation in **2** and **3** leads to a decrease of about 25 cm^{-1} in P=O and 75–85 cm^{-1} in C=C stretching frequencies with respect to the (*E*)-enol form **1c** of the free ligand and about 50 cm^{-1} in C=C stretching frequencies with respect to the (*Z*)-enol form **1b**.

The broad bands at 1562 (for **2**) and 1550 cm^{-1} (for **3**), including C=C and COO^- stretching vibrations, testify the presence of coordinated CH_3COO^- groups in both complexes. The same broad bands were observed in the spectra of the starting metal acetates. These data showed bidentate coordination by both COO^- and ligand **1**, the latter coordinating via P=O and hydroxyl oxygen atom of the enol form. It should be mentioned that the IR spectral characteristics of **2** and **3** concerning P=O and C=C stretching vibrations are in agreement with those of the Zn complex of **1**,[2] as well as of the metal complexes of diethyl ester of 2-oxopropanephosphonic acid $(EtO)_2P(O)CH(R)COCH_3$ when R=H or CN.[4,5]

In order to obtain some information on the stereochemistry of the complexes, EPR and magnetochemical measurements were performed, too. It was proven that both complexes are EPR silent. The magnetochemical (Figure 2) and electronic reflectance data (Figure 3) obtained for Co(II) complex **2** (pink colour) are indicative for octahedral stereochemistry.[6-8]

TABLE I

Selected IR data (nujol; ν/cm^{-1}) for the ligand **1** and its complexes **2**, **3**, and **4**

Ligand **1**	Co complex **2**	Ni complex **3**	Cu complex **4**	Ass
1020	1020	1020	1015	$\nu_{P—O—C}$
1050	1050	1050	1030	
1165[a]	1178	1175	1165	$\nu_{P=O}$
1200[b]			1200	
1405	1420	1420	—	$\nu_{C—O}$
1600[a]	1562	1550	1550	$\nu_{C=C}$
1635[b]				
2770[b]	—	—	—	$\nu_{O—H}$

[a] In (*Z*)-enol **1b**.
[b] In (*E*)-enol **1c**.

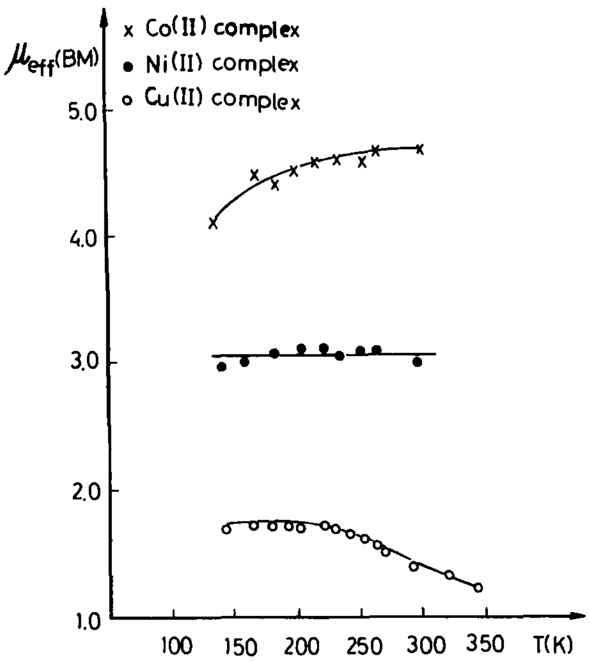


FIGURE 2 Temperature dependence of μ_{eff} for the Co(II), Ni(II) and Cu(II) complexes (2, 3 and 4 resp.); ($\mu_{eff} = 2.828\sqrt{\chi_M \cdot T}$).

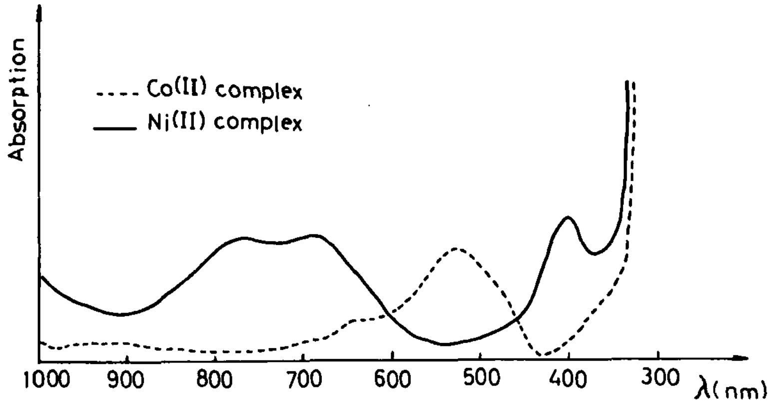


FIGURE 3 Electronic reflectance spectra of the Co(II) and Ni(II) complexes (2 and 3 resp.).

It is well documented that the Co(II) ground state in octahedral symmetry is $^4T_1$ and due to orbital contribution the effective magnetic moment is temperature dependent. Taking into account that the value of spin-orbit coupling constant for Co(II) (Oh) is $\lambda = -172$,[7] the expected μ_{eff} value should vary from 4.89 to 5.20 BM for the 140–298 K temperature range. For the complex **2** the μ_{eff} is indeed temperature dependent (Figure 2), its values being lower. This fact is due most likely to deviations from the regular octahedral symmetry.

The Ni(II) complex **3** (green colour) had μ_{eff} value of 2.93 BM at ambient temperature and no temperature dependence was observed (see Figure 2) in the range 130–300 K. These data together with the fact that it showed no EPR signal (both at ambient and low temperatures) indicated octahedral geometry of the complex **3** (most likely distorted one).

The Co(II) and Ni(II) complexes show low solubility. For that reason their electronic reflectance spectra were recorded. The data obtained (Figure 3) are in agreement with the stereochemistry proposed.[8]

The complex **2** is soluble only in DMSO, while the complex **3**, is not soluble in most of the organic solvents. The solution of **2** in DMSO (conc. $4.29.10^{-3}$ M; 1 = 2 cm) shows maximum at $\lambda = 550$ nm, corresponding to the transition $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$. The location of this maximum as well as the low value of ε (51 $l/mol^{-1} cm^{-1}$) correspond to the supposition for octahedral structure.[8]

If we assume that the cobalt and nickel ions are octahedrically coordinated and the phosphonyl and acetate ligands are bidentate we have to propose that these compounds exist not as monomeric molecules but in some polymeric forms (Figure 4) similar to those of the Co(II)- and Ni(II)-complexes of β-dicarbonyl compounds.[8]

The low solubility of **2** and **3** in organic solvents is in agreement with this supposition.

The copper complex **4** was obtained using copper acetate monohydrate in water-methanol solution (ratio ligand:acetate 2:1) at elevated temperature as a yellow crystalline solid, soluble in polar organic solvents (THF, methanol and chloroform). The elemental analysis proved the ligand:metal ratio to be 2:1. The solubility and the experimental value of the molecular weight (535 ± 26.80, THF, 45°C) showed that the copper complex **4** exists in monomeric form. Its IR spectral characteristics were similar to these of cobalt and nickel complexes **2** and **3**. The μ_{eff} value however is lower (Figure 2) than expected for mononuclear Cu(II) complex (1.9–2.0 BM); this fact might be attributed to intermolecular exchange interactions. It is well

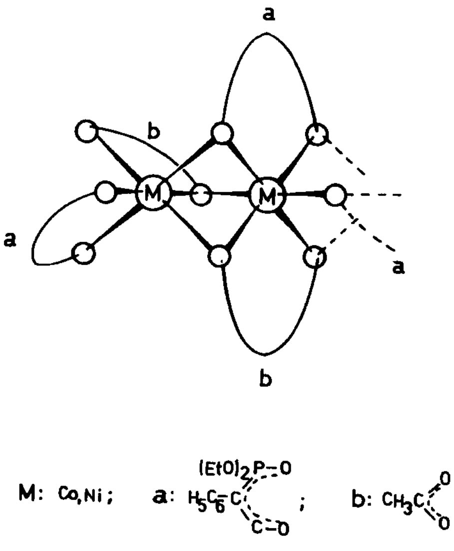


FIGURE 4 Possible polymeric structure of Co(II) and Ni(II) complexes (2 and 3 resp.).

TABLE II

EPR data for the Cu(II) complex **4**

T(K)	Solvent	g_{iso}	$A_{iso}^{1,2}$ ±2	g_{II} ±0.01	$g_{\perp}$ ±0.01	A_{II}(Oe) ±2	g'
100–160	$CHCl_3$	2.08[a]	—	2.18	~2.03	120	~2.00
240	$CHCl_3$	2.11[a]	—	2.15	~2.09	—	~2.07
293–303	$CHCl_3$	2.16	56	—	—	—	~2.08
233	THF	2.13[b]	—	—	—	—	—
293	THF	2.15	40	—	—	—	~2.10
100–160	CH_3OH	2.17[a]	—	2.36	2.08	124	~2.00
213	DMSO	2.17[a]	—	2.35	2.08	120	—

[a] Calculated values ($g_{iso} = {}^{2/3}g_{\perp} + {}^{1/3}g_{//}$).
[b] Singlet EPR signal only is observed.

documented that the existence of these interactions is leading both to lower magnetic moment and its temperature dependence.

Information concerning the structure of monomeric Cu(II) complex **4** formed in solution was obtained using the EPR method. For this purpose its EPR spectra in various solvents (chloroform, methanol, THF and DMSO) were recorded and the data obtained summarized in Table II.

The EPR data showed the existence of two different Cu(II) complex species in solution. The first one in frozen solutions has two-component anisotropic EPR signal with $g_{II} > g_{\perp}$, typical for square-planar Cu(II) stereochemistry.[9] [The g-component is exhibiting 4-component hyperfine structure due to $^{63,65}Cu$ (I = 3/2)]. Taking into account that its g-values are solvent dependent (in methanol and DMSO, which are possessing stronger coordination capacity, rather different g-values are observed in comparison with chloroform and THF solutions) square-planar structure could be accepted. The latter might be considered as distorted tetrahedral as well.

At the same time both at low and high temperatures a second signal with $g \sim 2$ is observed (partially overlapping with $g_{\perp}$-component of the other signal). This signal might be ascribed to an octahedral complex where the ligand is acting as tridentate one because of the participation of one ester oxygen atom (P—O—C) in coordination. One indication for this assumption is the IR spectrum of **4**, containing bands for two different P=O groups and stronger coordinated P—O—C groups (see Table I).

EXPERIMENTAL

The electronic and IR spectra were recorded on spectrometers "Specord UV-Vis", VSU-2P (VEB Carl Zeiss, Jena) and "Specord IR-71." The EPR spectra were obtained on the X-band spectrometer ERS 220 (GDR) (g-marker DPPH) equipped with a thermostat. The magnetic susceptibility measurements were performed in the temperature range 150 ÷ 300 K in argon atmosphere according to the Faraday method. The ligand **1** (diethyl-[2-oxo-1-phenylethyl]phosphonate) was sythesized by literature method.[3] The reaction of **1** and Co(II) and Ni(II) acetates was carried out in argon atmosphere using anhydrous methanol as solvent.

2-Diethoxyphosphonyl-2-phenyl-ethen-1-olato-cobalt-acetate (**2**). $Co(OOCCH_3)_2 \cdot 4H_2O$ (0.44 g, 1.75 mmol) in 6 cm^3 anhydrous methanol was added dropwise to a solution of **1** (0.99 g, 3.86 mmol) in 6

cm^3 anhydrous methanol. The reaction mixture was stirred for 2 hours at room temperature and left overnight. The precipitate was filtered off and stirred 1 hour with 10 cm^3 methanol. After filtration it was washed with methanol (2 cm^3) and ether (3 cm^3) and dried in vacuum to give pale pink crystalline solid of **2** (0.50 g, 77%) with m.p. 270 ÷ 272°C. The complex **2** is soluble in DMSO and insoluble in ether, chloroform, methanol, THF and water.

$C_{14}H_{19}O_6PCo$ (373.21) Calc. %: C, 45.06; H, 5.12; Co, 15.79. Found %: C, 45.40; H, 5.06; Co, 15.67.

2-Diethoxyphosphonyl-2-phenyl-ethen-1-olato-nickel-acetate (**3**). $Ni(OOCCH_3)_2 \cdot 4H_2O$ (0.44 g, 1.75 mmol) in 5 cm^3 anhydrous methanol was added dropwise to a solution of **1** (0.99 g, 3.86 mmol) in 4 cm^3 anhydrous methanol. The reaction mixture was stirred for 2 hours at room temperature and left overnight. After concentration the precipitate was filtered off, washed by stirring with 4 cm^3 water and dried in vacuum to give pale green crystalline solid **3** (0.52 g, 82%). The complex **3** does not melt up to 300°C. It is not soluble in DMSO, chloroform, methanol, THF, water, diglyme, acetonitrile and pyridine.

$C_{14}H_{19}O_6PNi$ (372.97) Calc. %: C, 45.09; H, 5.13; Ni, 15.74. Found %: C, 44.93; H, 5.36; Ni, 15.42.

Bis-(2-diethoxyphosphonyl-2-phenyl-ethen-1-olato)-copper (**4**). $Cu(OOCCH_3)_2 \cdot H_2O$ (0.30 g, 0.15 mmol) in 4 cm^3 water is added dropwise to a solution of **1** (0.84 g, 3 mmol + 10% excess) in 2 cm^3 methanol. The reaction mixture is heated 5 min. at 30°C, stirred 5 hours at room temperature and left overnight. The yellow crystalline solid was filtered off, washed with 5 cm^3 ether and dried in vacuum to give **4** (0.30 g, 40%) with m.p. 164 ÷ 166°C. The complex **4** is soluble in chloroform, methanol and THF and insoluble in hexane, water and ether.

$C_{24}H_{32}O_8P_2Cu$ (574.01) Calc. %: C, 50.23; H, 5.61; Cu, 11.07. Found %: C, 49.86; H, 5.68; Cu, 10.93. Ebulioscopic molecular weight (in THF) 535 ± 26.8 D.

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