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Structural and spectroscopic characteristics of α-cyano-substituted α-phosphoryl(thiophosphoryl)acetonates in neutral chelate-bridged complexes. Crystal structure of $[Cu[(PrO)_2P(O)C(CN)C(Me)O]_2]$*

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A comparative study of the three-dimensional and electronic structures of the chelate salts (ML_n) of enol forms of α-cyano-substituted α-phosphoryl- and α-(thiophosphoryl)acetones $(RO)_2P(X)C(CN)C{=}CMe(OH)$ (X = O or S; R = Pr or Et) with the Cu^I, Cu^{II}, and Co^{II} cations was carried out. In all complexes under consideration, the geometry of the central moiety of the O—C(Me)—C(CN)—P chelate-bridging ligand remains unchanged. The substantial electron delocalization involving the cyano group is observed in the O—C—C(CN)—P(X) ligand framework. The structure of the bis-chelate $Cu[(PrO)_2P(O)C(CN)C(O)Me]_2$ complex was established by X-ray diffraction analysis at 180 K and vibrational (IR and Raman) spectroscopy. The study in the temperature range from 290 to 140 K revealed the phase transition at 200 K accompanied by a change in the coordination polyhedron about the copper cation from a symmetrical octahedron (4+2 coordination) to a strongly unsymmetrically distorted octahedron (4+1+1 coordination). In both crystal modifications, four oxygen atoms form the base of the octahedron, and the axial positions are occupied by the nitrogen atoms.

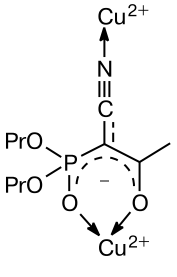
Key words: phosphoryl(thiophosphoryl)acylacetonitriles, enols, Co^{2+}, Cu^{2+}, and Cu^+ complexes, X-ray diffraction analysis, IR spectroscopy, Raman spectroscopy.

Products of acylation of (thio)phosphorylacetonitriles, which can formally be considered as α-cyano-substituted α-phosphoryl- and α-thiophosphoryl ketones $RR'P(X)CH(CN)C(O)R''$ (X = O or S; R,R′ = Alk, AlkO, or Ar; R″ = Alk or Ar), occur as enols $RR'P(X)C(CN)C{=}CR''OH$ (HL) both in the individual state and in solutions and belong to medium-strength monobasic OH-acids (their acidities are as high as or even higher than the acidities of carboxylic acids).[1—4] This enables one to prepare the corresponding chelate salts ML_n in good yields by neutralization of enols HL with metal oxides or hydroxides.[5,6]

Anions of these compounds are potentially tridentate (P=X, C—O⁻, and C≡N donor centers). The mode of coordination of the ligand can vary depending on the electron density delocalization in the ligand framework and the nature of both the X atom and cation.

In the present study, we carried out a comparative investigation of the chelate salts of two enols, *viz.*, $(PrO)_2P(O)C(CN){=}C(Me)OH$ (HL^1) and $(EtO)_2P(S)C(CN){=}C(Me)OH$ (HL^2),* with the aim of obtaining information on the structural features and electronic structures of phosphoryl and thiophosphoryl ligands of this type in neutral chelate-bridged complexes.

The three-dimensional and electronic structure of the salt CuL^1_2 (**1**) was established by X-ray diffraction analy-



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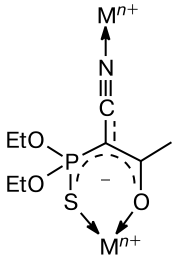

2, **3**

$M^{n+} = Co^{2+}$ (**2**), Cu^+ (**3**)

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* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

* Since both compounds can formally be considered as the enol forms of α,α′-disubstituted acetone, compounds of this group, which differ by substituents at the phosphorus atom, are denoted as CPA (cyanophosphorylacetone) and CTPA (cyanothiophosphorylacetone).

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sis and vibrational (IR and Raman) spectroscopy. The salts CoL^2_2 (**2**) and CuL^2 (**3**) have been studied by us earlier.[5,6] In all three complexes, the ligands are tridentate and fulfil a chelate-bridging function.

Experimental

Materials and reagents. Solvents were purified according to known procedures. Solutions for spectroscopic studies were prepared by the volume-weight method.

3-Cyano-3-dipropoxyphosphorylprop-2-en-2-ol, $(PrO)_2P(O)C(CN)=CMeOH$ (HL^1), was synthesized and purified according to a procedure described earlier.[1] Copper(II) acetate (chemically pure) was used without additional purification.

The CuL^1_2 salt (**1**) was prepared according to a procedure described earlier.[7,8] The melting point and elemental analysis data are consistent with the published data.[7] Attempts to record the NMR spectra of solutions of salt **1** failed because the complex is paramagnetic. Single crystals suitable for X-ray diffraction analysis were grown by isothermal evaporation of a solution of **1** in ether.

The IR spectra of solid samples and their solutions in CCl_4 and MeOH were measured on a Nicolet Magna IR-750 Fourier spectrometer; the resolution was 2 cm^{-1}.

The Raman spectra of single crystals and powders of the complexes were recorded on a Jobin Yvon T-64000 spectrometer, $\lambda = 514.5$ nm.

The optical absorption spectra (in Nujol mulls) were measured on a Specord M-40 spectrometer.

X-ray diffraction analysis. Pale-green platelet-like crystals of CuL^1_2 (**1**) $C_{20}H_{34}CuN_2O_8P_2$ (M = 555.97) are monoclinic, at 180 K $a = 9.329(1)$, $b = 13.312(2)$, $c = 10.186(2)$ Å, $\beta = 90.36(3)°$, $V = 1265(2)$ Å^3, $d_{calc} = 1.460$ g cm^{-3}, space group $P2_1$, $Z = 2$.

The X-ray diffraction data were collected on a Bruker SMART 1000 CCD diffractometer equipped with a low-temperature Oxford Cryosystems Cryostream Cooler attachment. To prevent cracking of the single crystal used, the temperature was reduced at a rate of 20 K h^{-1} (crystal-to-detector distance 3.960 cm, ω-scanning mode, frame width 0.3°, scan rate 20 s). The scaling corrections for absorption and detector area were applied with the use of the SADABS program[9] (T_{min}/T_{max} 0.332/0.802). The X-ray data were processed using the SAINT program.[10]

The complete experimental data set consisting of 14564 reflections ($2\theta_{max} = 54.06°$), which were collected from a single crystal of dimensions 0.10×0.30×0.50 mm at 180 K, was freed from an impurity component with the use of the RLAT[11] and GEMINI programs.[12] The unit cell parameters were determined and refined based on each of three frames (in the regions $\varphi = 0$, 120, and 240°). After averaging of equivalent reflections, 5479 reflections were obtained (2866 independent reflections, $R_{int} = 0.1291$). The high value of R_{int} reflects the presence of a residual impurity component attributed to the fact that the crystal from which the X-ray data were collected already began to crack. The completeness of the data set was 99.3%.

The structure was solved by direct methods and refined by the full-matrix least-squares method based on F^2_{hkl} with anisotropic thermal parameters for nonhydrogen atoms. The hydrogen atoms were placed in calculated positions and refined isotropically using the riding model with $B_{iso}(H) = nB_{eq}(C)$, where $B_{eq}(C)$ are the equivalent thermal parameters of the carbon atoms to which the corresponding hydrogen atoms are bound, $n = 1.2$ and 1.5 for the CH_2 and CH_3 groups, respectively. All calculations were carried out using the SHELXTL PLUS 5 program package.[13]

The final reliability factors were as follows: $R_1 = 0.0617$ (calculated based on F_{hkl} for 2687 reflections with $I > 2\sigma(I)$), $wR_2 = 0.1545$ (calculated based on F^2_{hkl} for a total of 2866 reflections), 298 parameters were refined, GOOF was 1.044, the Flack parameter was 0.08(2).

Results and Discussion

The structure of the phosphoryl-substituted complex CuL^1_2 (**1**) has been established earlier by X-ray diffraction experiment at 292 K.[8] However, the results of X-ray diffraction analysis were inaccurate (errors in the P—C bond lengths were up to 0.02 Å and errors in the C—C, C—O, and C—N bond lengths were up to 0.015 Å). Hence, there was good reason to refine the structure of complex **1** at low temperature with the aim of adequately comparing the geometric parameters of the complexes under study (it should be noted that the structures of the complexes CoL^2_2 (**2**) and CuL^2 (**3**) have been established by us earlier[5,6] with rather high accuracy at 163 and 110 K, respectively).

In attempting to carry out X-ray diffraction analysis at 110 K, it appeared that the crystal of CuL^1_2 completely decomposed. Hence, the study was carried out in the temperature range of 290—140 K. The unit cell parameters measured at 290 K are identical with those determined earlier[8] at 292 K (structure **A**). A decrease in the temperature to 230 K led to an anisotropic contraction of the unit cell, *i.e.*, the *b* and *c* parameters (and the unit-cell volume) decreased (Table 1), whereas the *a* parameter remained unchanged. At 200 K, crystals began to crack (turned opaque) and completely decomposed at 140 K.

Table 1. Changes in the unit cell parameters[a] of the CuL^1_2 complex (**1**) in the temperature range of 290—170 K

Parameter	290 K	260 K	230 K	200 K[b]	170 K[c]
a	9.564(3)	9.563(2)	9.569(3)	9.545(4)	9.313
b	13.396(5)	13.322(3)	13.248(4)	13.120(6)	13.115
c	10.595(3)	10.549(2)	10.504(3)	10.494(4)	10.144
β	90.23(3)	90.18(2)	90.25(3)	91.37(3)	90.06
V	1357(3)	1341(6)	1331(6)	1314(5)	1239

[a] The parameters of the monoclinic unit cell were determined based on 450—500 reflections measured in the range $2\theta = 0—28°$ on a Bruker SMART 1000 CCD diffractometer.

[b] The crystal began to crack.

[c] The errors were not calculated, and the data are tentative because they were obtained for a strongly cracked crystal.

Apparently, the structural transformation from **A** (at room temperature) to **B** (at low temperature) started at about 200 K. This transformation should be considered as an order—disorder phase transition. It is accompanied by a lowering of the monoclinic symmetry $P2_1/c \rightarrow P2_1$ (loss of a center of symmetry) with no multiplication of the unit cell. The authors of the study[8] noted that the OPr groups in the structure **A** were poorly located and they were refined with constraints on the C—O and C—C bond lengths. The resulting thermal ellipsoids of the atoms of these groups were much larger than those of the remaining atoms of the molecule. This is indicative of a possible disorder of the OPr groups at room temperature. At low temperature, these groups are ordered.

X-ray diffraction analysis of the low-temperature modification of the $\mathrm{CuL}^1{}_2$ complex was carried out at 180 K.

Description of structure. The structure of $\mathrm{CuL}^1{}_2$ at both room temperature (**A**) and 180 K (**B**) consists of the bis-chelate molecules linked in layers, which are parallel to the *ab* plane passing through the bridging CN groups. In the structure **B**, the nitrogen atoms occupy coordination sites 5 and 6 in the strongly unsymmetrically distorted octahedron of the copper atom (coordination 4+1+1) (Fig. 1). The distortion of the octahedron is characterized by the following angles: O(8)—Cu(1)—O(5), 93.2(2)°; O(5)—Cu(1)—O(4) and O(8)—Cu(1)—O(1), 87.7(2)°; O(8)—Cu(1)—N(1A), 85.7(2)°; O(8)—Cu(1)—N(2A), 95.3(2)°; O(4)—Cu(1)—N(1A), 96.2(2)°; O(4)—Cu(1)—N(2A), 82.9(2)°. The N(1A) and N(2A) atoms are arranged orthogonally to the $\{\mathrm{CuO_4}\}$ plane. The N(1A)—Cu(1)—N(2A) angle is 177.5(2)°.

The base plane of the octahedron is formed by four oxygen atoms (the oxygen atoms and the copper atom are coplanar to within 0.003 Å). The Cu—O bonds in one of the chelate rings (O(1)......O(4)) are somewhat longer (1.969(4) and 1.974(6) Å) than those in another ring (O(5)......O(8)) (1.939(4) and 1.951(4) Å). The O...O distances are 2.818(7) and 2.827(7) Å. The remaining bond lengths in both chelate rings are virtually equal (Table 2).

The main difference between the structures **A** and **B** is that the Cu...N distances in the structure **A** have equal values (molecule lies on a center of symmetry), whereas these distances in the structure **B** are substantially different (2.516 Å in **A**; 2.411 and 2.648 Å in **B**).

The chelate rings are nonplanar. In the structure **B**, the folding angles along the O(1)......O(4) and O(5)......O(8) lines are 29.5(2) and 20.9(3)°, respectively. In the structure **A**, the corresponding angle is 21.7°. The nonequivalence of the Cu—O bond lengths and the different folding angles of the chelate rings in the structure **B** can be related to the difference in the orientation of the CN group with respect to the $\{\mathrm{CuO_4}\}$ base plane. Thus, the N(1A) atom involved in a shorter contact with the copper atom is inclined toward the O(8) atom, the N(1A)—Cu(1)—O(8) angle is 85.7°, whereas the re-

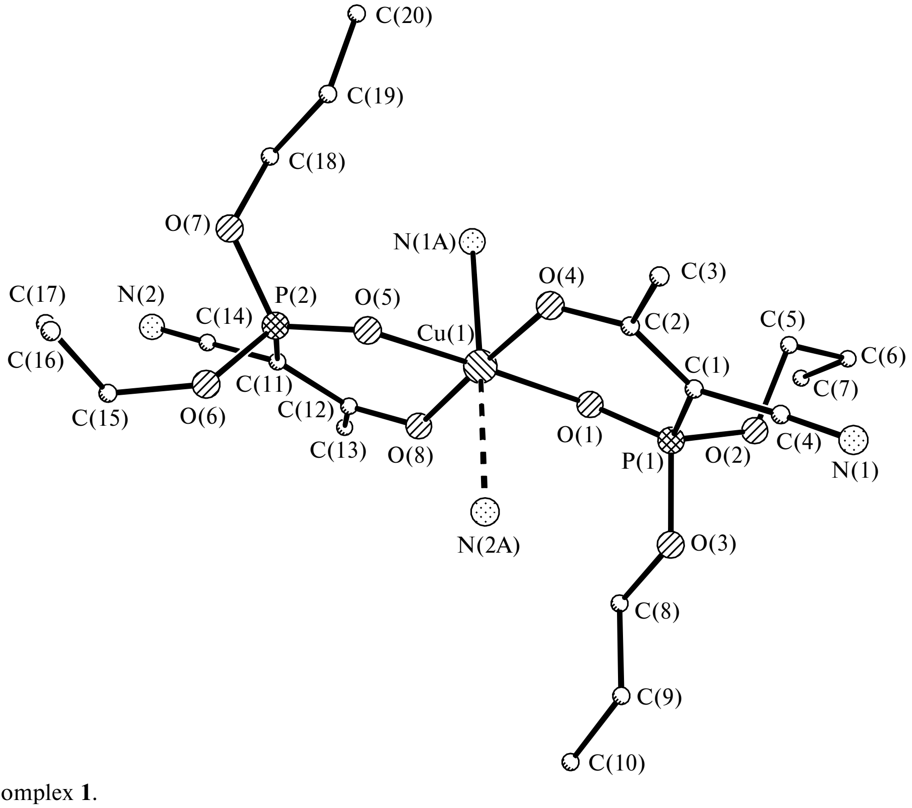

Fig. 1. Structure of complex **1**.

Table 2. Principal bond lengths (*d*/Å) in the central O—P—C(CN)—C—O fragment of some enol forms of cyano-substituted phosphoryl- and thiophosphorylacetones (HL) and their complexes

Compound	HL	*T*/K	*d*/Å						References
			P—O	P—C	C=C	C—O	C—C(N)	C≡N	
			Neutral complexes						
CuL^1_2 (**1**)[a]	$(PrO)_2P(O)C(CN)=CMe(OH)$	180	1.490(5)	1.749(6)	1.424(8)	1.275(7)	1.418(8)	1.165(8)	[b]
			1.494(5)	1.759(6)	1.432(8)	1.268(7)	1.416(8)	1.147(8)	
		292	1.484(8)	1.73(2)	1.40(1)	1.27(1)	1.40(1)	1.15(1)	8
CoL^2_2 (**2**)	$(EtO)_2P(S)C(CN)=CMe(OH)$	163	1.96(1)[c]	1.755(3)	1.410(5)	1.266(4)	1.409(4)	1.149(4)	5
CuL^2 (**3**)	$(EtO)_2P(S)C(CN)=CMe(OH)$	110	1.990(1)[c]	1.745(3)	1.414(4)	1.255(4)	1.403(4)	1.143(4)	6
			Anionic complex						
$Na[ZnL^3_3]$	$(EtO)_2P(O)C(CN)=CMe(OH)$	292	1.476(8)	1.723(9)	1.40(1)	1.24(1)	1.45(1)	1.13(1)	16
			Individual enols						
HL^4	$Me(Pr^iO)P(O)C(CN)=CMe(OH)$[d]	153	1.489(1)	1.792(2)	1.377(2)	1.320(2)	1.425(2)	1.147(2)	3
HL^5	$Ph_2P(O)C(CN)=CMe(OH)$[e]	153	1.501(2)	1.787(2)	1.377(2)	1.326(2)	1.427(2)	1.151(2)	23
HL^6 [a]	$Ph_2P(S)C(CN)=CMe(OH)$[e]	293	1.965(2)[c]	1.799(4)	1.368(6)	1.330(6)	1.425(6)	1.145(6)	2
			1.968(2)	1.801(3)	1.359(6)	1.325(6)	1.419(6)	1.136(7)	

[a] The data for two independent molecules are given.

[b] The present study.

[c] The parameters for the bond involving the sulfur atom.

[d] Intermolecular hydrogen bond.

[e] Intramolecular hydrogen bond.

maining N(1A)—Cu(1)—O angles are much larger (91.1—96.2°). The N(1A) atom is more uniformly surrounded by the O atoms of the bis-chelate system compared to the N(2A) atom. The N(1A)......O(1), N(1A)...O(4), and N(1A)......O(5) bond lengths have close values (3.145(7), 3.147(7), and 3.130(7) Å, respectively), and the N(1A)......O(8) distance is somewhat shorter (2.978(7) Å). By contrast, the N(2A).........O(4) and N(2A)...O(5) distances are shorter than the N(2A).........O(1) and N(2A)...O(8) distances (the corresponding values are 3.098(7), 3.195(7), 3.335(7), and 3.423(7) Å).

In molecule **1**, the P—O bond lengths in the chelate rings have equal values (P(1)—O(1) and P(2)—O(5) are 1.490(5) and 1.494(5) Å, respectively) and are somewhat larger than the average bond length* in the uncoordinated fragments (1.449(7) Å in $(C—O)_3—P=O$ and 1.489(10) Å in $C_3—P=O$).[14] Data on only four metal complexes with ligands of this type,[16—19] *viz*., $Na[ZnL^1_3]$, $Mg_3[(EtO)_2P(O)CH=C(Me)O]_6$, $(NO_3)_2Co_2[(EtO)_2P(O)CH=C(CH_2NC_5H_{10})O]_2$, and $Cl_2MoO_2[(EtO)_2P(O)CH_2C(=O)Ph]$, are available in the Cambridge Structural Database (CSD).[15] In spite of the fact that the ligands in these complexes are present both as anion and neutral species and, in addition, the PO group in the $Na[ZnL^1_3]$ complex is coordinated to two metal atoms (Zn and Na), the P—O bond lengths have close values (1.476; 1.471, 1.475, and 1.485; 1.488; 1.483 Å, respectively). Hence, the P=O→M coordination to the metal atom, like hydrogen bonding,[20] leads to only a slight change in the P=O bond length. The vibrational frequency of the PO group is a much more sensitive characteristic in both cases (both upon coordination and hydrogen bonding;[20] spectroscopic data are given below). In addition, an elongation of the PO bond may also be indicative of its involvement in conjugation.

The P—C distances (1.749(6) and 1.759(6) Å) correspond to the one-and-a-half order bond.[21] The C—C bond lengths (1.424(8) and 1.432(8) Å) and C—O bond lengths (1.275(7) and 1.268(7) Å) are close to the corresponding typical bond lengths in acetylacetonate complexes with delocalized bonds in the chelate ring (1.40—1.42 Å and 1.25—1.30 Å).[22] Hence, the interatomic distances in the central fragment of the P—C—C—O ligand correspond to one-and-a-half order bonds, like in the cobalt(II) and copper(I) thiophosphoryl complexes described earlier[5,6] (see Table 2), which is evidence for the bond delocalization in this fragment. The CN group is also involved in delocalization, as judged from a shortening of the C—C(N) bonds (1.418(8) and 1.416(8) Å) compared to the standard value[14] (1.431(14) Å). The bond length in the CN group itself is generally noninformative and poorly correlates with the involvement of the CN group in coordination and conjugation. In the complex under consideration, this bond is only slightly elongated (1.165(8) and 1.147(8) Å) compared to the average value[14] (1.136(10) Å).

The remaining bond lengths in complex **1** are typical of the corresponding fragments.[14] The atomic coordi-

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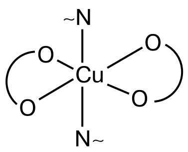
* The reference P—O bond length in the uncoordinated $C(C—O)_2P=O$ fragments is lacking, and the neutral ligand HL^1 was not structurally studied.

nates and complete crystallographic characteristics of the structure of **1** were deposited with the Cambridge Structural Database.

Comparison of results of X-ray diffraction analysis. In neutral complexes **1—3**, the ligand fulfils the chelate-bridging function being coordinated by the PX, CO^-, and CN groups. However, these complexes have different three-dimensional structures:



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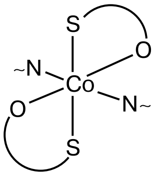

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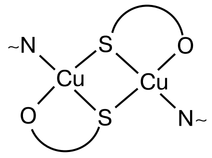

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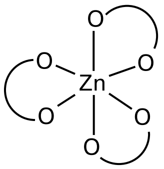
In all cases, the electron density delocalization involving the CN group occurs in the ligand framework. In spite of the differences in the structure and nature of the substituents at the P atom (P=O or P=S), the geometry of the —P—C(CN)—C—O fragment (or, broader, of —P—C(CN)—C(Me)—O) in the compounds under study remains virtually unchanged to within the experimental error (see Table 2).

The selected bond lengths in the central fragment of the neutral complexes containing the anionic ligand L^-, the anionic $Na[ZnL^1{}_3]$ complex, and, for comparison, the neutral enols RR´P(X)C(CN)=CMeOH (X = O or S) are given in Table 2.

Let us consider the CPA-based $Na[ZnL^3{}_3]$ anionic complex for comparison.[16] In this complex, the trigonally distorted octahedron about the Zn atom is formed by six oxygen atoms of three identical chelate rings.



The bridging oxygen atoms of the PO groups are coordinated to the Zn and Na ions. The coordination environment about the Na cation is formed by three bridging phosphoryl oxygen atoms of the complex anion and three nitrogen atoms of the cyano groups of the adjacent complex anions. The geometry of the chelate-bridging ligand in this complex is analogous to that in the above-considered neutral complexes. However, unlike the above-considered compounds, the Na countering rather than the central 3d cation is involved in an additional coordination with the CN group giving rise to a 3D framework. Apparently, this is the reason for the fact that the C—CN bond length (1.45(1) Å) is less shortened than those in the neutral complexes (1.403(4)—1.418(8) Å). The P—C bond, which is very sensitive to the involvement of the P=X group in coordination,[5,6,16] is somewhat less elongated. This is, apparently, indicative of a weaker coordination of the P—O group to the Zn cation in the anionic complex compared to that in the neutral complexes with the 3d cation (see also the spectroscopic data). On the whole, the distribution of the bond lengths (P=O, 1.476(8) Å; P—C, 1.723(9) Å; C—C, 1.40(1) Å; C—CN, 1.45(1) Å; C—O, 1.24(1) Å; C≡N, 1.13(1) Å) is consistent with the bond delocalization in the P—C—C—O fragment involving the cyano group.

The bond lengths in the central fragment of the ligand of the $[ZnL^3{}_3]^-$ complex anion (see Table 2), which are close to the average values for the neutral salts ML_n, are also indicative of conjugation, in spite of the fact that the charge distribution in the anion leads to certain differences in the geometry (apparently, associated with a poorer accuracy of the determination of the bond lengths in $Na[ZnL^3{}_3]$).[16]

It was of interest to compare the structures of the complexes under consideration with those of the starting enols HL^1 and HL^2. However, the data on the latter structures are lacking in the CSD.[15] The closest analogs are the $Me(Pr^iO)P(O)C(CN)=C(Me)OH$ (HL^4),[3] $Ph_2P(O)C(CN)=C(Me)OH$ (HL^5),[23] and $Ph_2P(S)C(CN)=C(Me)OH$ (HL^6)[2] molecules. In the solid state, all these enols occur as the *Z* isomers stabilized by either an intermolecular hydrogen bond in the first compound or an intramolecular O—H...X=P hydrogen bond (X = O or S) in two other cases.

A comparison of the bond lengths and bond angles[3] in the structures of the free enols (see Table 2) showed that the geometry of the Me(OH)C=C(CN)—P fragment in these compounds remains unchanged in spite of the different types of H bonds and different substituents at the phosphorus atom. However, the geometry of this fragment in the free enols differs from that in the above-considered complexes.

Hence, the X-ray diffraction data demonstrated that the geometry of the central fragment is retained within groups of individual molecules HL and neutral 3d metal complexes ML_n (or, with certain qualifications, of 3d metal enolate complexes) in all the structures under consideration based on cyano-substituted phosphoryl- and thiophosphorylacetones. In all cases, the electron density delocalization involving the CN group occurs in the ligand framework. As expected, the degree of conjugation is higher in the structures, in which the metal cation is coordinated by ionic ligands and in which all three donor centers, *viz.*, PX, CO, and CN, are involved in coordination, rather than in a neutral molecule, where the O—H...O bonds are covalent or partially covalent.[23]

Table 3. Data from vibrational spectroscopy (ν/cm^{-1}) of complexes **1**—**4** and enols HL

Compound	ν(P=X)	ν(C=C—O)[a]	ν(C≡N)
HL^1, *E* isomer	1240[b]	1610[b]	2215[b]
HL^1, *Z* isomer	1190	1600	2215
$K^+(L^1)^-$	1230[b]	1550[b]	2180[b]
$[CuL^1{}_2]$	1170	1523	2193
	(1165[b])	(1520[b])	(2190[b])
HL^2, *E* isomer	630[b]	1616[b]	2209[b]
HL^2, *Z* isomer	603	1580	2209
$[CoL^2{}_2]$[5]	625	1521	2220, 2210[c]
	(625[b])	(1525[b])	(2192[b])
$[Cu_2L^2{}_2]$[6]	590	1527	2192
HL^3, *E* isomer	1240[b]	1610[b]	2215[b]
HL^3, *Z* isomer	1192	1608	2215
$Na[ZnL^3{}_3]$[16]	1180	1530	2189

[a] Mixed ν(C=C) + ν(C=O$^-$) vibration in the complexes.

[b] A solution in MeOH.

[c] The in-phase and antiphase vibrations.

Vibrational spectra. To analyze the character of the electron density distribution in cyano-substituted phosphoryl- and thiophosphorylacetonates, we compared the vibrational spectra of complex **1** with the spectra of complexes **2**, **3**, and **4** described earlier,[5,6,16] and each spectrum was compared with the spectrum of the corresponding enol. The frequencies of the most informative spectral lines belonging to vibrations of the functional P=X, C=C—O, and CN groups are given in Table 3.

Earlier, we have demonstrated[1,2] that the individual enol forms of CPA and CTPA adopt *Z* configurations stabilized by either an intramolecular hydrogen bond (cyclic *Z* isomer) or an intermolecular P=X...H—OC hydrogen bond (linear *Z* isomer). In solutions, CPA and CTPA exist as mixtures of two geometric isomers of the *Z*- and *E*-enol forms.[3,4] According to the ^{31}P NMR spectroscopic data,[3] the ratio between the *Z* and *E* isomers in a methanolic solution of enol HL^1 is 79 : 21. This is consistent with the data from IR spectroscopy. Thus, the IR spectrum has two P=O stretching bands and two C=C stretching bands, whereas the C≡N stretching band is unsplit. The IR spectrum of a methanolic solution of enol HL^1 shows absorption bands ν(P=O) at 1240 and 1190 cm^{-1} assigned to the free P=O group (linear *Z* and *E* isomers) solvated by the solvent and the P=O group involved in intramolecular hydrogen bonding (cyclic *Z* isomer), respectively. The formation of an intramolecular hydrogen bond leads to a lowering of the C=C bond order in the *Z* isomer, which is characterized by the ν(C=C) frequency of 1600 cm^{-1}, whereas the *E* isomer of enol HL^1 is characterized by a ν(C=C) band at 1610 cm^{-1}. In the IR and Raman spectra of the individual enol, the ν(P=O) and ν(C=C) vibrational frequencies characterize the *Z* isomer (see Table 3). It should be noted that the P=S...HO intramolecular interaction present in enol HL^2 leads to a more substantial lowering of the C=C bond order compared to that observed in the the phosphoryl compound HL^1. In the spectra of the *Z* and *E* isomers, the ν(C=C) bands are observed at 1580 and 1616 cm^{-1} (see Refs. 5 and 6). The vibrational frequencies ν(P=S) of enol HL^2 are 603 and 630 cm^{-1} for the thiophosphoryl group involved in hydrogen bonding and the free group, respectively[5,6] (see Table 3).

In the case of complex **1**, the coordination causes a decrease in the P=O vibrational frequency to 1173 cm^{-1} (Fig. 2), *i.e.*, the coordination bond between the oxygen atom of the P=O group and the divalent copper atom is stronger than the H bond in the *Z* isomer of the free enol. By contrast, the coordination of the sulfur atom to the Co^{2+} cation in complex **2** has virtually no effect on the vibrational frequency of the P=S bond (see Table 3), whereas the ν(P=S) frequency is lowered by ~25 cm^{-1} upon the formation of an intramolecular hydrogen bond in the *Z* isomer[5] (see Table 3). The bifurcate coordination to the copper(I) cation in complex **3** causes an even more substantial decrease in the ν(P=S) frequency (40 cm^{-1}; see Table 3).

The vibrational spectra of the complexes containing the enolate anions should be compared not only with the spectra of the starting enols HL^1 and HL^2 but also with the spectra of acetyl- and phosphorylacetonates, which have been studied in detail by different methods, including the normal coordinate analysis.[24—27] It was found that vibrations of the acetonate chain are mixed. The intense absorption bands characteristic of most of the complexes are observed in the regions of 1520—1570 and 1350—1450 cm^{-1} and belong to the ν(C—C) + ν(C—O) and ν(C—C) + $\delta(CH_3)$ vibrations, respectively.[24,26,28] Correspondingly, the IR spectrum of complex **1** has an intense band at 1527 cm^{-1}. An analogous (but weak) line is observed in the Raman spectrum (Fig. 2). In the IR spectra of complexes **2** and **3**, the same band is observed at 1521 and 1523 cm^{-1}, respectively. The spectrum of complex **4** shows this band at 1530 cm^{-1} (see Table 3). Apparently, the similarity of the ν(C—C) + ν(C—O) vibrational frequencies for all four complexes indicates that neither the strength of coordination of the P=X group nor the nature of the substituent X have a substantial effect on the redistribution of the bond orders in the C=C—O group. The bands at 1368 and 1334 cm^{-1} in the spectrum of complex **1** and at 1388 cm^{-1} in the spectra of complexes **2** and **3** can be assigned to ν(C—C) + $\delta(CH_3)$ vibrations of the acetonate chain.[24,26]

The changes in the spectroscopic characteristics of the cyano group induced by coordination are of particular interest. Upon coordination of the nitrogen atom (or the formation of the C≡N...H hydrogen bond[29]), the ν(C≡N) vibrational frequency of the cyano group increases by 20—40 cm^{-1} as the coordination is strengthened and the

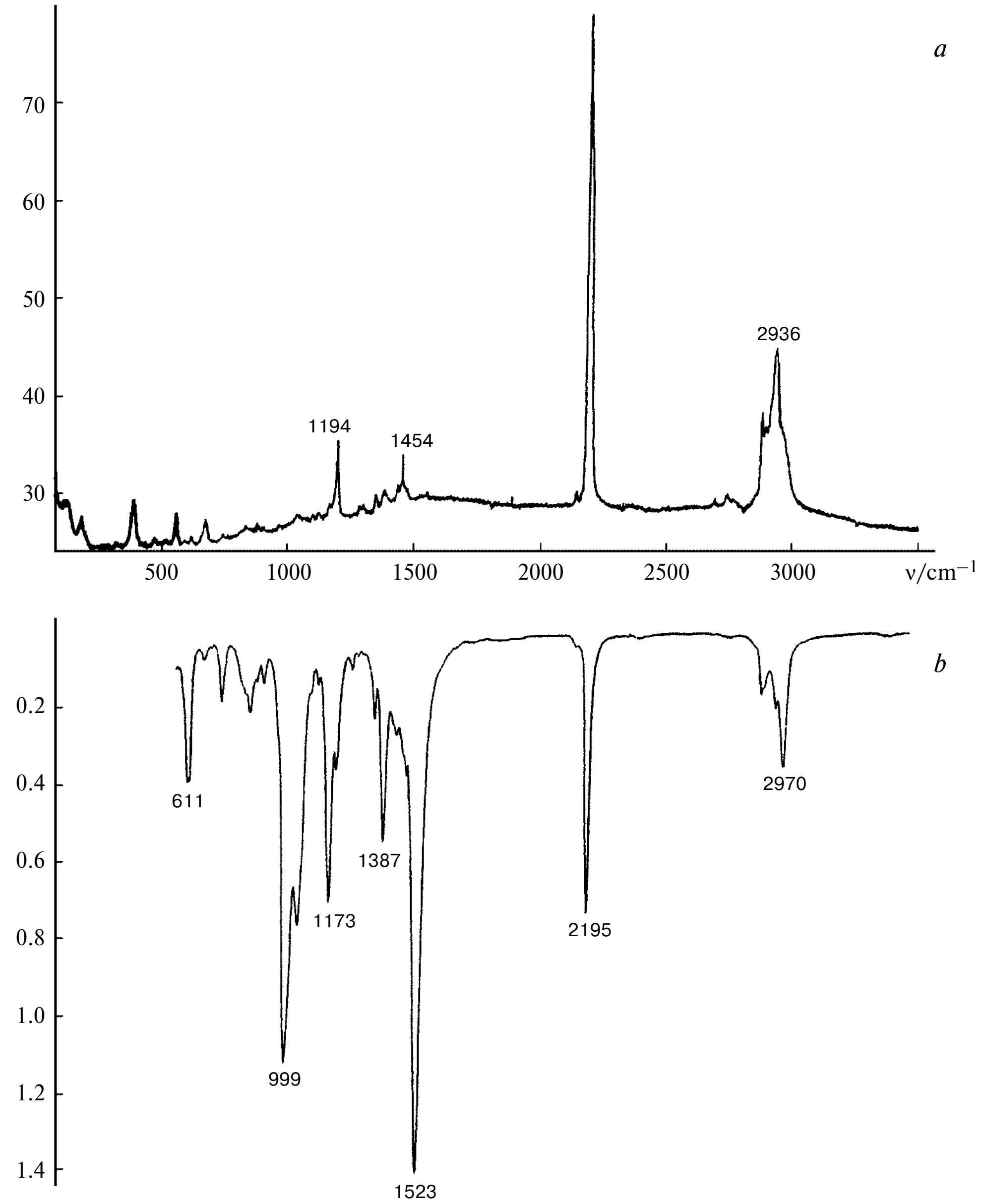


Fig. 2. Raman (*a*) and IR (*b*) spectra of complex **1**.

charge of the coordinating cation increases.[24] At the same time, delocalization of the negative charge in the enolate anion leads to a decrease in the vibrational frequency of the cyano group. In the spectrum of enol HL^1, this band is observed at 2215 cm^{-1}, whereas in the spectrum of the corresponding enolate anion the frequency decreases to 2180 cm^{-1} (IR spectra of solutions of the enol and its potassium salt $K^+(L^1)^-$ in MeOH).

In the IR spectrum of complex **1**, the ν(C≡N) vibration is observed at 2195 cm^{-1}. This band has a weak low-frequency shoulder (2190 cm^{-1}), which may be associated with either a vibrational interaction between two axially arranged cyano groups or the Davydov splitting. This band corresponds to an intense Raman line at 2190 cm^{-1}. Hence, the vibrational frequency of the CN bond in the spectrum of complex **1** is higher than that in the spectrum of the free anion $(L^1)^-$ by only ~10 cm^{-1}. It can be assumed that in solutions of complex **1**, the coordination of the CN group to the copper cation (through which the layers are linked) is destroyed, which should lead to a lowering of the ν(C≡N) frequency. However, the expected shift of the ν(C≡N) band was not observed in the spectra of solutions of complex **1** in MeOH and CCl_4. Apparently, the axial bond in the tetragonal copper complex, which is elongated due to the Jahn—Teller effect, too slightly influences the ν(C≡N) frequency. In the spectrum of complex **2**, which is characterized by a stronger equatorial coordination of the CN group compared to that in complex **1**, the ν(C≡N) vibrational frequency is higher than its value for the anion by ~35 cm^{-1} (2215 cm^{-1} for the crystalline complex compared to 2180 cm^{-1} for the potassium salt)[5] (see Table 3). Dissolution of complex **2** leads to the cleavage of the coordination bond between the Co^{2+} cation and the N atom, as evidenced by the lowering of the ν(C≡N) frequency to 2190 cm^{-1}. Hence, using complex **2** as an example, it is possible to estimate the dependence of the ν(C≡N) frequency on two factors, *viz.*, delocalization of the negative charge in the L$^-$ anion (~10 cm^{-1}) and coordination of the nitrogen atom (~25 cm^{-1}).

In the spectrum of complex **3** characterized by the strongest coordination of the CN group to the copper(I) cation, the vibrational frequency ν(C≡N) is 2192 cm^{-1}, *i.e.*, it is lower than that in the spectrum of complex **2**, which may be associated with the lower charge of the coordinating cation.

It should be noted that the spectrum of complex **4** in which the N atom of the cyano group of the $[ZnL^3{}_3]^-$ complex anion is weakly coordinated to the sodium cation[16] (ionic bond) has a CN vibration band at 2189 cm^{-1}, which is only slightly different from that in the spectra of complexes **1** and **3**.

Hence, there are at least three reasons for a change in the frequency of the quasilocal stretching vibration of the CN group in the complexes under consideration, *viz.*, the electron density delocalization (involvement of the CN group in conjugation), the strength of coordination of the nitrogen atom, and the charge of the coordinating cation. This hinders the use of the shifts of the ν(C≡N) band as a criterion for the coordination of the nitrogen atom.

Since there is no unambiguous correlation with the change in the vibrational frequency ν(C≡N), the intensities of the corresponding Raman lines serve as essential characteristics, because the intensities of these lines increase sharply upon complex formation. The stronger (according X-ray diffraction analysis) is the coordination of the nitrogen atom, the higher are the intensities. The most intense line ν(C≡N) corresponds to complex **3**. This band is 15 times more intense than the CH vibrational line (2930 cm^{-1}) chosen as the internal standard, whereas the intensities of these lines in the spectrum of the free enol are approximately equal. For complex **2**, this ratio is 9, whereas this ratio for complex **1** is a mere 3. The only known fact of an increase in the intensity of the Raman line of the CN group with increasing strength of the CN...H bond was observed for cyano-substituted carboxylic acids.[29]

It is known[30] that the intensities of Raman lines depend on different factors, among which are the preresonance (close values of the wavelength of the exciting laser line and the wavelength UV absorption of the molecule), the symmetry of the UV transition and observed vibration, and the state of the sample under consideration. It should be noted that the absorption band of enols (π→π* transition) in the region of 39000 cm^{-1} (frequency of the exciting laser line of 19436 cm^{-1} provides conditions for the preresonance[30]) is shifted upon dissociation of the proton and coordination of the anions to within 2%, which may not substantially change the conditions of preresonance. It should be emphasized that only the intensity of the CN vibrational band substantially increases in the spectra of both a single crystal and powder. In addition, according to the X-ray diffraction data, the geometric characteristics of the N≡C—C—C—O fragment are approximately identical in all three complexes and, consequently, these complexes are characterized by the same symmetry of the electron and vibrational transitions. Therefore, this geometry cannot account for the differences in the intensities of the lines in the Raman spectra of three complexes.

Hence, an increase in the intensity of the Raman line belonging to the ν(C≡N) vibration upon coordination of the nitrogen atom may be associated with an increase in the polarizability of the C≡N bond and can serve as a criterion for the coordination of the nitrogen atom of the cyano group in studies of the structures of these complexes.

The comparative spectroscopic study of complexes **1—3** demonstrated that the electron density delocalization in the central fragment of the ligand is independent of both the nature of the coordination center at the phosphorus atom (X atom) and the strength of its coordination. Since the CN group is also involved in conjugation, the change in its vibrational frequency cannot serve as reliable evidence for coordination of the nitrogen atom. It is worthy of note that coordination of the CN group leads to a substantial increases in the intensity of its Raman line.

To summarize, the comparative X-ray diffraction and spectroscopic study of the neutral chelate-bridged complexes with ligands based on α-cyano-substituted α-phosphoryl- and α-thiophosphorylacetones showed that the three-dimensional and electronic structure of the central fragment of the ligand is virtually independent of the nature of the substituent at the phosphorus atom (PO or PS), the nature of the metal atom, and the structure of the complex. In all cases, a substantial electron density delocalization involving the CN group is observed in the ligand framework.

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