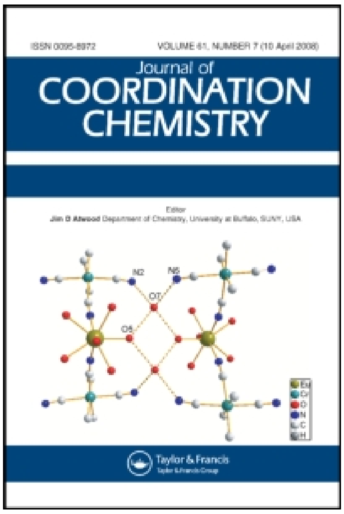

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Olyana Angelova[a]; Josef Macíček[b]; Galin Petrov[a]
[a] Department of Chemistry, University of Sofia, Sofia, Bulgaria [b] Institute of Applied Mineralogy. Bulgarian Academy of Sciences, Sofia, Bulgaria

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SPECTROSCOPIC AND X-RAY STRUCTURAL CHARACTERIZATION OF SODIUM TRIS(3-CYANO-2,4-PENTANEDIONATO)ZINCATE(II) ETHANOLATE AND SODIUM TRIS(DI-*O*-ETHYL 1-CYANO-2-OXO-PROPYLPHOSPHONATO)ZINCATE(II) AND RELATED ANIONIC COMPLEXES

OLYANA ANGELOVA*
Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

JOSEF MACÍČEK
Institute of Applied Mineralogy, Bulgarian Academy of Sciences, 1000 Sofia, Bulgaria

and GALIN PETROV
Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

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Two series of complexes of the type NaM(CNacac)$_3$, M = Ni, Zn, and NaM(CNpaac)$_3$, M = Co, Ni, and Zn have been prepared and characterized by IR spectroscopic and X-ray powder and single-crystal diffraction methods. Each series has been found to be isostructural. The crystal and molecular structures of the title complexes NaZn(CNacac)$_3$.EtOH (**1**) and NaZn(CNpaac)$_3$ (**2**) have been determined. Crystal data (**1**): $M = 506.78$, monoclinic, $P2_1/n$, $a = 14.450(2)$, $b = 11.873(1)$, $c = 15.407(2)$ Å, $\beta = 117.06(2)°$, $V = 2354(1)$ Å^3, $Z = 4$, $D_x = 1.427$g.cm^{-3}, $F(000) = 1045$, $R = 0.045$ and $R_w = 0.047$. (**2**): $M = 742.87$, cubic, $P\bar{4}3n$, $a = 19.464(6)$ Å, $V = 7374(4)$ Å^3, $Z = 8$, $D_x = 1.338$g.cm^{-3}, $F(000) = 3088$, $R = 0.051$ and $R_w = 0.067$. Both structures contain pairs of tris-chelated ZnL$_3^-$ anions and Na counterions sharing common faces of their coordination polyhedra. The additional coordination of the CN-groups results in the formation of 3D-networks.

Keywords: Cobalt, nickel, zinc, 3-cyano-2,4-pentanedione, di-*O*-ethyl 1-cyano-2-oxo-propylphosphonate, X-ray structures

INTRODUCTION

Recently we have shown that 3-cyano-2,4-pentanedione (CNacacH) and di-*O*-propyl 1-cyano-2-oxo-propylphosphonate (CNpaacH) contained similar backbone fragments, O=C–C(CN)–C=O and O=P–C(CN)–C=O, respectively, and formed stable neutral ML$_2$ complexes with some divalent 3d-metal ions.[1–3] In these compounds the ligands perform both *O,O*-chelating and partially[2] or fully[1,3] CN-bridging functions. Here we report on the characterization of ionic species of the type

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* Author for correspondence.

ML_3^-, where M = Ni, Zn for L = CNacac and Co, Ni, Zn for L = CNpaac. The structures of NaZn(CNacac)$_3$.EtOH (1) and NaZn(CNpaac)$_3$ (2) have been solved.

EXPERIMENTAL

Measurements

IR spectra were measured on a Specord 75M spectrophotometer in nujol mulls with KBr windows. Analytical data were obtained from the Microanalytical Laboratory at the Chemistry Department, University of Sofia. Melting temperatures were measured on a Stanton Redcroft differential scanning calorimeter. X-ray powder diffraction patterns were measured on DRON UM1 diffractometer with CoKα radiation (FeKβ filter) calibrated with external Ge standard.

Synthesis of ligands

The NaCNacac salt was synthesized according to Fackler.[4] CNpaacH was obtained by the following procedure. Some 7.8 cm^3 (0.05 mol) of diethyl cyanomethylphosphonate were added to a solution of 1.2 g (0.07 mol) NaH in THF (approx. 150 cm^3) cooled to −60°C under stirring for 1 hour. Some 3.5 cm^3 (0.05 mol) of acetylchloride were added dropwise to the grey-white suspension. The addition was completed in 1 hour under a dry nitrogen atmosphere and then the temperature was allowed to rise slowly. During this process the colour of the suspension turned yellow (at −40°C), white (at −30°C) and brownish-grey (at room temperature). The mixture was left overnight. After removing the solvent, the white residue was treated with 6 M HCl. The organic layer was separated and the aqueous phase extracted with ether and dichloromethane. Combined organic phases were dried over Na_2SO_4, concentrated, and again treated with 6 M HCl. The above procedure was repeated and the orange-red organic phase distilled under vacuum. The fraction boiling at 88–92°C (0.6–0.7 mm Hg) was collected. Yield 4.5 g (42% with respect to diethyl cyanomethylphosphonate), $\eta_D^{25} = 1.4515$. Anal.: Calc. for $C_8H_{14}NO_4P$: C, 43.83; H, 6.41; N, 6.40%. Found: C, 43.78; H, 6.50; N, 6.34%. Characteristic IR bands: ν(CN), 2208(s); ν(C–C–O), 1605(s); ν(P=O), 1270(s); ν(P–OR), 1020–60(s) cm^{-1}. The NaCNpaac salt was prepared by reaction with NaH in equimolar quantities.

Synthesis of NaML$_3$ complexes

All complexes were prepared in a similar way by a metal-exchange reaction between the Na salts of the ligands and the corresponding anhydrous metal chlorides. MCl_2 (0.005 mol) and excess Na salt of the ligand (0.015 mol) were mixed in approx. 150 cm^3 of carefully dried and freshly distilled ethanol at room temperature. The mixtures were left overnight. The resulting precipitates were dissolved in a series of portions of hot ethanol in order to separate the NaCl residue. After evaporation of the solvent the complexes were recrystallized from dry ethanol. Table I contains essential data from chemical and spectroscopic analyses.

X-ray data collection

The experimental details and relevant crystallographic data for (1) and (2) are

TABLE I
Chemical and spectroscopic data for the complexes.

	Colour	M.P.	Elementary analysis		
			C(f/c)	H	N
NaNi(CNacac)$_3$.S*	grass-green	322	48.03/47.76	4.84/4.92	8.40/8.42
NaZn(CNacac)$_3$.S*	pale-yellow	271	47.43/46.98	4.78/4.84	8.30/8.23
NaCo(CNpaac)$_3$	pink-violet	257	39.14/38.88	5.34/5.07	5.71/5.83
NaNi(CNpaac)$_3$	yellow-green	266	39.16/38.75	5.34/5.35	5.71/5.69
NaZn(CNpaac)$_3$	colourless	235	38.80/38.61	5.29/5.22	5.66/5.67

	Selected IR bands, cm^{-1}					
	ν(CN)	ν(C-C-O)	ν(P=O)	ν(P-O-C)	ν(O-C-C)	$\delta(CH_3)+\nu(M-O)$
NaNi(CNacac)$_3$.S*	2220vs	1620vs				616m
NaZn(CNacac)$_3$.S*	2200vs	1620vs				618m
NaCo(CNpaac)$_3$	2185vs	1535vs	1173vs	1030–60vs	967s	612s + 593s
NaNi(CNpaac)$_3$	2187vs	1540vs	1177vs	1030–60vs	970s	613s + 598s
NaZn(CNpaac)$_3$	2189vs	1530vs	1180vs	1030–60vs	970s	617s + 598s

* A solvent molecule, here ethanol.

summarized in Table II. Inspection of the systematic intensity extinctions for (**1**) ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) showed unambiguously the space group $P2_1/n$ and for (**2**) indicated possible space groups $P\bar{4}3n$ or $Pm\bar{3}n$. Empirical absorption corrections based on ψ-scans followed by Lorentz and polarization corrections were applied before averaging the symetry-equivalent reflections. The Enraf-Nonius CAD4SDP44M diffractometric system with CAD4 V5.0 and SDP/PDP V3.0 software[5] was employed. Atomic scattering factors and anomalous dispersion coefficients were used as coded in the SDP package.

Solution and refinement of the structures

The Zn atom in (**1**) was located from a Patterson map and used for initial phasing. Subsequent difference Fourier syntheses combined with full-matrix least-squares refinement (LSFM program) revealed the positions of all non-hydrogen atoms of the complex and indicated a highly disordered ethanol molecule. Any trials to find a plausible disorder scheme for the solvent remained unsuccessful. Therefore, restraints on the O–C–C backbone geometry were applied and the ethanol coordinates were further refined with the LSRE program to $R = 0.075$. The methyl hydrogen atoms in the complex were located from specially selected 2D sections of the 3D difference Fourier maps and refined as riding on the corresponding carbon atoms. Hydrogen atoms in the ethanol molecule were not located. The final cycle of the LSFM refinement gave $R = 0.045$ and $R_w = 0.047$. The highest peak in the final difference Fourier synthesis (0.916 e Å^{-3}) was closely positioned to the C(E1) atom and negative peaks did not exceed -0.47 e.Å^{-3}.

In the case of (**2**) the expected value for the density corresponded to $Z = 8$ and this directed our attention to the space group $P\bar{4}3n$ with the Zn atom disposed on a three-

TABLE II
Crystal data for (1) and (2).

	NaZn(CNacac)$_3$.EtOH	NaZn(CNpaac)$_3$
formula	$C_{20}H_{24}NaZnN_3O_7$	$C_{24}H_{39}NaZnN_3O_{12}P_3$
molecular weight	506.78	742.87
crystal dimensions, mm	0.2 × 0.4 × 0.58	0.6
crystal system	monoclinic	cubic
space group	$P2_1/n$	$P\bar{4}3n$
a, Å	14.450(2)	19.464(6)
b, Å	11.873(1)	
c, Å	15.407(2)	
β, °	117.060(2)	
V, Å^3	2354(1)	7374(4)
Z	4	8
d_c, g cm^{-3}	1.427	1.338
temperature, K	292	292
μ, cm^{-1}	11.3	8.7
$F(000)$	1045	3088
scan method	ω/2θ	ω/2θ
radiation	MoKα (λ = 0.71073)	
monochromator	graphite cryst	
scan speed range, deg min^{-1}	2–7	1–7
θ range, deg	28	24
hkl range	$+h, +k, \pm l$	$+h, +k, +l$
reflections (total)	6183	6390
reflections (unique)	3481	1084
R_{int}	0.025	0.032
reflections used, $I > 3\sigma(I)$	3297	715
R	0.045	0.051
R_w	0.047	0.067
final GOF	1.527	1.79
weighting scheme	unit weights	unit weights
max Δ/σ	2.55	0.70

fold axis in an eightfold special position. The coordinates for Zn were derived from the Patterson function. Further structure solution and refinement followed the general procedures applied to (1). All non-hydrogen atoms except the carbons of the ethoxy groups were found. Isotropic LSFM refinement converged at $R = 0.198$. Trials to refine the structure in the centrosymmetric space group $Pm\bar{3}n$ failed; $R = 0.438$. No attempts to lower the lattice symmetry were made because the merging factor, $R_{int}(I) = 0.032$ for the cubic point group $m\bar{3}m$, was reasonably good. The initial space group choice was therefore retained. Geometrical restraints were implied on the ethoxy carbon atoms and convergence gave $R = 0.089$. All atoms were allowed individual anisotropic thermal parameters and the final least-squares cycle gave $R = 0.051$ and $R_w = 0.064$. H atoms were not located. The final difference map showed maximum peaks smaller than 0.5 e Å^{-3} in the vicinity of the Zn atom, and close to the positions of the ethoxy carbon atoms.

The fractional coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms in (1) and (2) are given in Tables III and IV, respectively. Tables V and VI summarize selected bond lengths and angles. Figures 1 and 2 represent the

TABLE III
Fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in $NaZn(CNacac)_3.EtOH$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}(Å^2)
Zn	0.41595(4)	0.14110(5)	0.20308(4)	3.11(1)
Na	0.5532(1)	−0.0825(2)	0.2751(1)	3.94(5)
O(1)	0.5752(2)	0.1209(3)	0.2951(2)	3.39(7)
O(2)	0.4589(3)	0.2662(3)	0.1392(2)	4.09(9)
O(11)	0.4348(2)	0.0075(3)	0.1235(2)	3.88(8)
O(12)	0.2656(2)	0.1436(3)	0.0982(2)	4.07(8)
O(21)	0.3991(2)	0.0118(3)	0.2880(2)	3.93(8)
O(22)	0.3827(3)	0.2493(3)	0.2873(2)	3.91(8)
N(7)	0.8080(3)	0.3710(5)	0.2628(3)	5.3(1)
N(17)	0.1617(4)	−0.0795(5)	−0.1815(4)	6.0(1)
N(27)	0.3358(5)	0.1129(6)	0.5488(3)	7.8(2)
C(1)	0.6504(3)	0.1781(4)	0.3005(3)	3.0(1)
C(2)	0.5460(4)	0.3071(4)	0.1607(3)	3.5(1)
C(3)	0.6410(3)	0.2691(4)	0.2380(3)	3.2(1)
C(4)	0.7337(4)	0.3254(5)	0.2515(3)	4.0(1)
C(5)	0.7556(4)	0.1446(5)	0.3781(4)	5.0(1)
C(6)	0.5457(5)	0.4033(5)	0.0961(4)	6.8(2)
C(11)	0.3747(4)	−0.0276(4)	0.0406(3)	3.6(1)
C(12)	0.2227(4)	0.0928(4)	0.0187(3)	3.5(1)
C(13)	0.2717(4)	0.0123(4)	−0.0145(3)	3.4(1)
C(14)	0.2111(4)	−0.0381(5)	−0.1075(4)	4.3(1)
C(15)	0.4131(5)	−0.1203(7)	−0.0012(4)	6.1(2)
C(16)	0.1095(4)	0.1209(6)	−0.0458(4)	5.2(2)
C(21)	0.3766(3)	0.0187(5)	0.3572(3)	3.6(1)
C(22)	0.3632(3)	0.2304(5)	0.3571(3)	3.5(1)
C(23)	0.3628(3)	0.1224(5)	0.3952(3)	3.6(1)
C(24)	0.3453(5)	0.1171(6)	0.4793(4)	5.2(1)
C(25)	0.3619(4)	−0.0924(5)	0.3990(4)	7.1(2)
C(26)	0.3369(4)	0.3317(5)	0.4004(4)	6.6(2)
O(E)	0.4996(4)	−0.2672(4)	0.2448(5)	10.5(2)
C(E1)	0.411(1)	−0.306(1)	0.225(1)	18.7(6)
C(E2)	0.410(1)	−0.372(1)	0.282(1)	18.9(6)

$B_{eq} = \frac{4}{3}\sum_{i}\sum_{j}\beta_{ij}a_i.a_j.$

complex anions in (**1**) and (**2**), respectively, viewed along the Na . . . Zn axis, with the corresponding atom numbering schemes.

RESULTS AND DISCUSSION

IR spectroscopic data

A very sharp peak at 3410 cm^{-1} in $NaZn(CNacac)_3.EtOH$ and a broader one at 3380 cm^{-1} in $NaNi(CNacac)_3.EtOH$ is attributed to the stretching mode of the OH group from the solvent molecule.[6] The ν(CN) frequency in the ionic $NaM(CNacac)_3.EtOH$ complexes is lowered by 40 cm^{-1} in comparison with those of the neutral Co and $Ni(CNacac)_2$ complexes[3] (2240 cm^{-1}). In the ionic $NaM(CNpaac)_3$ complexes this frequency is further lowered by about 10–15 cm^{-1}, probably due to the smaller extent of ligand π-conjugation hindered by the presence of a phosphorus atom.

TABLE IV

Fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in $NaZn(CNpaac)_3$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq}(Å^2)
Zn	0.15867(5)	0.159	0.159	3.345(7)
Na	0.2515(2)	0.252	0.252	3.56(3)
P	0.2320(2)	0.0619(1)	0.2707(2)	4.81(6)
O(1)	0.1916(3)	0.0696(3)	0.1151(3)	4.2(1)
O(2)	0.2188(3)	0.1323(3)	0.2458(3)	3.8(1)
C(1)	0.2235(4)	0.0003(5)	0.2076(5)	3.8(2)
C(2)	0.2070(4)	0.0127(5)	0.1388(4)	3.9(2)
C(3)	0.2059(7)	−0.0494(5)	0.0888(5)	6.2(3)
N	0.2468(5)	−0.1234(4)	0.2493(4)	6.6(2)
C(4)	0.2359(6)	−0.0697(5)	0.2305(5)	5.1(2)
O(3a)	0.1851(6)	0.0414(4)	0.3338(4)	10.9(3)
O(3b)	0.3084(5)	0.0541(4)	0.2991(5)	10.7(2)
C(5a)	0.139(1)	0.076(1)	0.3637(9)	20.6(8)
C(5b)	0.3519(8)	0.0942(9)	0.331(1)	19.8(8)
C(6a)	0.101(2)	0.065(1)	0.405(1)	23(1)
C(6b)	0.4186(8)	0.087(1)	0.338(1)	16.6(7)

$B_{eq} = \frac{4}{3}\sum_i\sum_j \beta_{ij}a_i.a_j$.

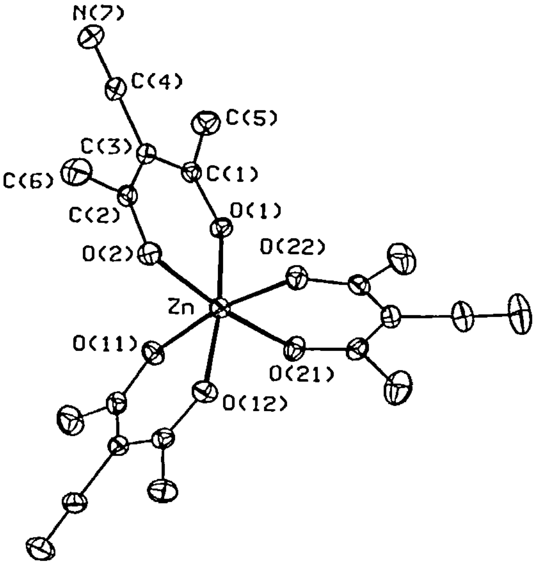


FIGURE 1 The complex anion $Zn(CNacac)_3^-$ with the atom numbering scheme. Only one enantiomer is shown.

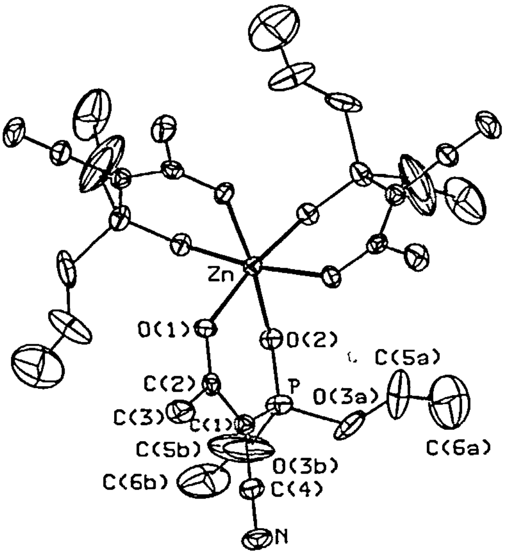


FIGURE 2 The complex anion Zn(CNpaac)$_3^-$ with the atom numbering scheme. Only one enantiomer is shown.

In the region of the valence stretching frequencies, lowering of both carbonyl ($\Delta\nu = -185\,\mathrm{cm}^{-1}$) and phosphoryl ($\Delta\nu = -93\,\mathrm{cm}^{-1}$) group vibrations is observed in agreement with the participation of those groups in chelation. The ionic CNacac complexes show one very strong band at 1620 cm^{-1} assigned to a mixed vibration of C=O and C=C stretches in the planar six-membered chelate rings.[6,7] The second strong band, typical for these stretches and appearing around 1530 cm^{-1} in the corresponding metal acetylacetonates,[7,8] becomes very weak in the present compounds. One good reason for this could be the influence of the CN-group, affecting the ν(C=C) vibrations more strongly than ν(C=O). As a result of the enhanced by the cyano-group π-electron delocalization, the two valence stretching frequencies are probably equivalized in energy and coincide in a broader band of complex shape. The presence of the phosphonate group in NaM(CNpaac)$_3$ causes a substantial lowering of the ν(C=C=O) band to 1530–1540 cm^{-1}.[9,10]

The ν(P=O) frequency at 1260 cm^{-1} in free ligands moves to 1190–1220 cm^{-1} in complexes with neutral ligands and further to 1150–1180 cm^{-1} in complexes with ionic ligands.[9,11–13] This large decrease in the P=O stretch was interpreted by Cotton and Schunn[9] as resulting from a lowering of the P=O bond order more than would be expected for simple coordination of the phosphoryl oxygen atom to the metal atom, and later by Seyden-Penne[14] as an evidence of lengthening of the P=O bond due to carbanion formation. Brunette *et al.*[12] first pointed out the close range of P=O stretching vibrations in metal complexes with β-ketophosphonates in neutral and anionic form. They proposed the existence of asymmetric delocalization of the negative charge on the chelate ring including the C–C–O fragment.

TABLE V

Interatomic distances (Å) and angles (°) in the structure of NaZn(CNacac)$_3$.EtOH.

Zn-Na	3.195(2)	C(1)-C(3)	1.411(7)
Zn-O(1)	2.096(3)	C(2)-C(3)	1.420(5)
Zn-O(2)	2.029(5)	C(11)-C(13)	1.418(6)
Zn-O(11)	2.097(4)	C(12)-C(13)	1.416(9)
Zn-O(12)	2.035(3)	C(21)-C(23)	1.416(8)
Zn-O(21)	2.102(4)	C(22)-C(23)	1.411(8)
Zn-O(22)	2.032(4)		
Na-O(E)	2.302(6)	C(1)-C(5)	1.498(6)
Na-O(1)	2.437(4)	C(2)-C(6)	1.515(8)
Na-O(11)	2.426(3)	C(11)-C(15)	1.50(1)
Na-O(21)	2.580(4)	C(12)-C(16)	1.516(6)
Na-N(7)	2.395(7)	C(21)-C(25)	1.525(8)
Na-N(27)	2.471(5)	C(22)-C(26)	1.504(9)
O(1)-C(1)	1.252(7)	C(3)-C(4)	1.426(7)
O(2)-C(2)	1.245(6)	C(13)-C(14)	1.427(6)
O(11)-C(11)	1.246(5)	C(23)-C(24)	1.431(9)
O(12)-C(12)	1.249(6)		
O(21)-C(21)	1.252(7)	O(E)-C(E1)	1.26(2)
O(22)-C(22)	1.251(8)	C(E1)-C(E2)	1.19(2)
N(7)-C(4)	1.143(8)	N(17)-O(E)	2.770(7)
N(17)-C(14)	1.145(7)		
N(27)-C(24)	1.140(9)		

O(1)-Zn-O(2)	85.9(1)	O(E)-Na-O(1)	169.2(2)
O(1)-Zn-O(11)	85.1(1)	O(E)-Na-O(11)	101.5(2)
O(1)-Zn-O(12)	170.4(2)	O(E)-Na-O(21)	101.9(2)
O(1)-Zn-O(21)	84.1(1)	O(E)-Na-N(7)	88.4(2)
O(1)-Zn-O(22)	98.4(1)	O(E)-Na-N(27)	94.2(2)
O(2)-Zn-O(11)	96.9(2)	O(1)-Na-O(11)	71.3(1)
O(2)-Zn-O(12)	93.2(1)	O(1)-Na-O(21)	68.1(1)
O(2)-Zn-O(21)	169.9(1)	O(1)-Na-N(7)	100.6(2)
O(2)-Zn-O(22)	93.5(2)	O(1)-Na-N(27)	91.4(2)
O(11)-Zn-O(12)	85.6(1)	O(11)-Na-O(21)	68.1(1)
O(11)-Zn-O(21)	83.9(1)	O(11)-Na-N(7)	99.7(2)
O(11)-Zn-O(22)	169.3(2)	O(11)-Na-N(27)	160.6(3)
O(12)-Zn-O(21)	97.0(1)	O(21)-Na-N(7)	165.3(2)
O(12)-Zn-O(22)	91.2(1)	O(21)-Na-N(27)	97.5(2)
O(21)-Zn-O(22)	86.4(2)	N(7)-Na-N(27)	92.1(3)
O(1)-C(1)-C(3)	123.9(3)	O(1)-C(1)-C(5)	116.4(4)
O(2)-C(2)-C(3)	124.9(5)	O(2)-C(2)-C(6)	114.8(4)
O(11)-C(11)-C(13)	123.7(6)	O(11)-C(11)-C(15)	117.5(4)
O(12)-C(12)-C(13)	125.1(4)	O(12)-C(12)-C(16)	116.3(6)
O(21)-C(21)-C(23)	123.4(6)	O(21)-C(21)-C(25)	116.3(5)
O(22)-C(22)-C(23)	124.4(5)	O(22)-C(22)-C(26)	116.1(5)
C(3)-C(1)-C(5)	119.7(4)	C(1)-C(3)-C(4)	117.9(4)
C(3)-C(2)-C(6)	120.3(5)	C(2)-C(3)-C(4)	117.3(5)
C(13)-C(11)-C(15)	118.7(4)	C(11)-C(13)-C(14)	117.3(5)
C(13)-C(12)-C(16)	118.6(4)	C(12)-C(13)-C(14)	117.8(5)
C(23)-C(21)-C(25)	120.4(5)	C(21)-C(23)-C(24)	116.9(5)
C(23)-C(22)-C(26)	119.5(5)	C(22)-C(23)-C(24)	116.9(5)
C(1)-C(3)-C(2)	124.9(5)	N(7)-C(4)-C(3)	179.7(8)
C(11)-C(13)-C(12)	124.7(4)	N(17)-C(14)-C(13)	178.9(7)
C(21)-C(23)-C(22)	126.2(5)	N(27)-C(24)-C(23)	177.1(6)
O(E)-C(E1)-C(E2)	114(1)		

Numbers in parentheses are estimated standard deviations.

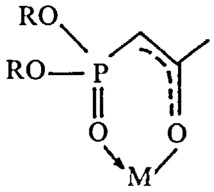


TABLE VI
Interatomic distances (Å) and angles (°) in the structure of NaZn(CNpaac)$_3$.

Zn–O(1)	2.035(6)	O(1)–C(2)	1.24(1)
Zn–O(2)	2.124(5)	C(1)–C(2)	1.40(1)
Na–O(2)	2.408(6)	C(1)–C(4)	1.45(1)
Na–N	2.435(9)	C(2)–C(3)	1.55(1)
P–O(2)	1.476(6)	N–C(4)	1.13(1)
P–C(1)	1.723(9)	O(3a)–C(5a)	1.26(2)*
P–O(3a)	1.581(9)	O(3b)–C(5b)	1.31(2)*
P–O(3b)	1.595(9)	C(5a)–C(6a)	1.11(3)*
		C(5b)–C(6b)	1.31(2)*
O(1)–Zn–O(1)^{i}	92.6(2)	O(2)–Na–O(2)^{i}	71.9(2)
O(1)–Zn–O(2)	87.3(2)	O(2)–Na–N^{iii}	106.1(3)
O(1)–Zn–O(2)^{i}	96.7(2)	O(2)–Na–N^{iv}	92.5(2)
O(1)–Zn–O(2)^{ii}	170.7(2)	O(2)–Na–N^{v}	164.2(3)
O(2)–Zn–O(2)^{i}	83.4(2)	N–Na–N	89.6(4)
O(2)–P–C(1)	113.3(4)	O(1)–C(2)–C(1)	124.6(8)
O(2)–P–O(3a)	112.9(4)	O(1)–C(2)–C(3)	117.4(7)
O(2)–P–O(3b)	111.4(4)	C(1)–C(2)–C(3)	118.0(8)
C(1)–P–O(3a)	108.8(4)	C(1)–C(4)–N	178(2)
C(1)–P–O(3b)	105.6(4)	P–O(3a)–C(5a)	130(1)
O(3a)–P–O(3b)	104.2(5)	P–O(3b)–C(5b)	135(1)
P–C(1)–C(2)	125.8(8)	O(3a)–C(5a)–C(6a)	135(3)
P–C(1)–C(4)	114.7(7)	O(3b)–C(5b)–C(6b)	129(2)
C(2)–C(1)–C(4)	119.6(8)		

* Disordered atoms. Symmetry codes: (i) z, x, y; (ii) y, z, x; (iii) $1/2 + y, 1/2 - x, 1/2 - z$; (iv) $1/2 - x, 1/2 - z, 1/2 + y$; (v) $1/2 - z, 1/2 + y, 1/2 - x$.

Again the influence of the CN substituent on the P=O stretch is not expected to be direct, but stronger substitution dependence (if any) should be pronounced in the P–C vibrations. The other intense bands in the region 1030–1060 and around 970 cm^{-1}, characteristic of organophosphorus compounds containing P–*O*-alkyl groups[15], are not significantly influenced by coordination and/or substitution by the cyano group in the P–*C*-alkyl fragment.

The assignment of the strong combined band around 600 cm^{-1} to $\delta(C–CH_3) + \nu(M–O)$[6–8] receives further support by the splitting, found in the CNpaac complexes, most likely originating from the difference of the phosphoryl and carbonyl M–O bond force constants.

X-ray powder data

The powder diffraction patterns of the NaM(CNacac)$_3$.EtOH, M = Ni, Zn, complexes showed that they are isomorphous. Attempts to index the patterns using the single-crystal unit cell parameters were troublesome. Nevertheless, the unit cell parameter values for NaNi(CNacac)$_3$.EtOH were refined[16] to $a = 14.725(5)$, $b = 11.857(3)$, $c = 15.252(4)$ Å, $\beta = 116.90(2)°$. NaM(CNpaac)$_3$, M = Co, Ni, Zn, complexes were also found to be isomorphous. Their powder diffraction patterns were accurately evaluated and have been deposited in the Powder Data File.[17] The corresponding unit cell parameters are 19.493(2) and 19.4253(8) Å for NaCo(CNpaac)$_3$ and NaNi(CNpaac)$_3$, respectively.

Crystal Structure of (1)

The structure of (**1**) consists of tris-chelated Zn(CNacac)$_3^-$ anions disposed in general positions, Na cations and disordered solvent molecules. The coordination octahedron of Zn is distorted towards a trigonal prism. The twist-angle, φ, between the "basal" triangular faces[18] (Fig. 1) is 49.8°. The oxygen atoms of one of these faces bridge Zn and Na ions; the average Zn–O(bridging) distance [2.098(4) Å] is longer than the corresponding non-bridging value [2.032(4) Å]. Such differences in the coordination bonds have been encountered in KCd(acac)$_3$.H$_2$O,[19] and in the trinuclear complex Zn(acac)$_2$.[20] The chelate O...O bite distances vary in the range 2.807(5)–2.830(5) Å; the non-bonding O...O distances between the bridging O atoms [2.807(6)–2.835(4) Å] are shorter than those between the non-bridging atoms [2.905(4)–2.957(6) Å].

The Na cation has a distorted octahedral environment consisting of three bridging O atoms, two N atoms from cyano groups of adjacent complex anions and one O atom belonging to a solvent molecule. The Na–N distances [2.395(7) and 2.471(5) Å] fall in the range of the Na–O distances [2.302(6)–2.580(4) Å]. The shortest Na–O distance is that to the solvent molecule. The N–Na–N angle is 92.1(3)° and all others deviate significantly from ideal octahedral values (Table V). The Na...Zn distance is 3.195(2) Å.

The ligands are planar to within 0.022, 0.065 and 0.092 Å; the fold angles along the O...O axes are 3.3, 7.4 and 2.9°, for the rings with increased atomic numbering respectively. No significant alteration of bond lengths in the three ligands occurs. Two of them have CN groups bonded to adjacent sodium ions, while the cyano group of the third one is found to be involved in H-bonding with the hydroxyl group of the solvent molecule [N(17)...O(E): 2.790(3) Å; C(14)–N(17)...O(E): 138.9(2)°]. Thus the solvent blocks the coordination site around Na ion for a further CN group. There are no other unusual intermolecular distances between the non-hydrogen atoms less than 3.5Å.

Crystal structure of (2)

The Zn(CNpaac)$_3^-$ anion and Na cation in the structure of (**2**) are disposed on a threefold axis. The Zn atom has a trigonally distorted octahedral environment of oxygen atoms of the three chelating ligands. The twist-angle φ = 52°.[18] The phosphoryl oxygen atoms bridge the Zn and Na ions. The Zn–O bond lengths are 2.035(6) and 2.124(5) Å, respectively for the non-bridging and bridging groups. The order of increase for the non-bonding O...O distances around the Zn atom is as follows: 2.827(8) Å between the bridging phosphoryl groups, 2.872(8) Å for the bite distance of the ligand, and 2.941(8) Å between the non-bridging carbonyl oxygen atoms. The bite angle is 87.3(2)°.

The Na ion is surrounded octahedrally by three bridging oxygen atoms from the complex anion and three cyano nitrogen atoms of adjacent complex anions. The Na–O distance of 2.408(6) Å is shorter than the Na–N at 2.435(9) Å. The O(2)–Na–O(2) angle, 71.9(2)°, is significantly smaller than the ideal value of 90° for the octahedron. The Na... Zn distance is 3.12(1) Å.

TABLE VII
Selected bond lengths (Å) in several representative phosphonate and β-ketophosphonate compounds.

	O=P	P–C	C–C	C–O	Ref.*
Individual compounds					
L^aH	1.451(6)	1.832(7)			1
L^bH	1.456(3)	1.829(3)			2
L^cH	1.471(7)	1.812(9)			3
L^dH	1.459(3)	1.816(3)	1.552(5)	1.436(4)	4
Complexes with neutral ligands					
$Er(L^eH)_2(NO_3)_3.H_2O$	1.479(6)	1.789(8)	1.518(11)	1.239(11)	5
$Sm(L^eH)_2(NO_3)_3$	1.480(2)	1.784(4)	1.518(4)	1.261(3)	5
$Er(L^fH)_2(NO_3)_3.H_2O$	1.469(4)	1.792(7)	1.518(11)	1.231(9)	6
	1.476(5)	1.786(8)	1.523(9)	1.232(8)	
$UO_2(L^eH)_2(NO_3)_3$	1.485(5)	1.782(8)	1.501(11)	1.260(8)	7
$Th(L^gH)_2(NO_3)_3$	1.478(4)	1.787(6)	1.509(8)	1.256(6)	8
$MoO_2(L^eH)Cl_2$	1.487(2)	1.788(3)	1.503(4)	1.262(3)	9
Complexes with ionic ligands					
$CoL^h(NO_3)$	1.490(8)	1.739(9)	1.335(12)	1.314(12)	10
CoL^i_2	1.464(5)	1.727(9)	1.363(11)	1.304(9)	11
MgL^i_2	1.486(5)	1.731(9)	1.343(11)	1.315(10)	12
	1.471(5)	1.732(9)	1.358(13)	1.299(10)	
	1.474(6)	1.695(8)	1.385(11)	1.341(10)	
CuL^j_2	1.484(8)	1.73(2)	1.40(1)	1.27(1)	13
$NaZnL^j_3$	1.476(6)	1.723(9)	1.399(12)	1.236(11)	14

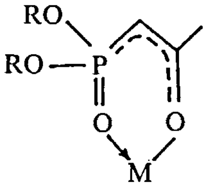
L^aH: *O,O*-dimethyl 1-hydroxy-2,2,2-trichloroethylphosphonic acid; L^bH: *O,O*-diethyl bis(*p*-chlorophenoxy)methylphosphonic acid; L^cH: 3-hydroxy-3-dimethylphosphono-2,2,5,5-tetramethyltetrahydrofuran; L^dH: *O,O*-diethyl 2-hydroxy-1,2-phenylethylphosphonic acid; L^eH: diisopropyl *N,N*-diethylcarbamylmethylenephosphonate; L^fH: diisopropyl 1,2-bis(*N,N*-diethylcarbamyl)ethylphosphonate; L^gH: diethyl *N,N*-diethylcarbamylmethylenephosphonate; L^hH: γ-piperidino-β-ketophosphonate; L^iH: paacH; L^jH: CNpaacH. * 1: E. Hohne and K. Lohs, *Z. Naturforsch. B*, **24**, 1071 (1969); 2: S. Kuple and I. Seidel, *Krist. Techn.*, **15**, 149 (1980); 3: G. Samuel and R. Weiss, *Tetrahedron*, **26**, 2995 (1970); 4: Unpublished data; 5: reference 24; 6: reference 25; 7: S.M. Bowen, E.N. Duesler and R.T. Paine, *Inorg. Chem.*, **22**, 286 (1983); 8: S.M. Bowen, E.N. Duesler and R.T. Paine, *Inorg. Chem*, **21**, 261 (1982); 9: S.M. Bowen, E.N. Duesler, D.J. McCabe and R.T. Paine, *Inorg. Chem.*, **24**, 1191 (1985); 10: M.T.R. Youinou, J.E. Guerchais, M.E. Louer and D. Grandjean, *Inorg. Chem.*, **16**, 872 (1977); 11: reference 21; 12: reference 23; 13: reference 1; 14: this work.

Similar tris-coordination was reported earlier for the trinuclear bis(diethyl 2-oxopropylphosphonato) complexes of Co(II),[21] Ni(II),[22] and Mg(II).[23] These species can be considered as having the structural formula $M[M(paac)_3]_2$, *i.e.*, they represent an associate of a central bivalent M(II) cation with two terminal monovalent tris-coordinated anions. It is noteworthy that the two types of complexes,

$M[M(paac)_3]_2$ and $NaM(CNpaac)_3$, differ in the origin of the bridging O atoms. In $M[M(paac)_3]_2$ the carbonyl groups are common for two metal ions while in $NaM(CNpaac)_3$ the phosphoryl groups participate. A tentative explanation of the latter could be the more pronounced coordination affinity of P=O with respect to that of C=O donor site of the ligand. Support for this assumption is the coordination mode of another type of ligands, also containing the O=C–C–P=O fragment, found in the structures of bis(diisopropyl *N*,*N*-diethylcarbamylmethylenephosphonate)erbium(III) nitrate monohydrate[24] and bis(diisopropyl [1,2-bis(*N*,*N*-diethylcarbamyl)ethyl]phosphonate)-erbium(III) nitrate monohydrate.[25] Only the phosphoryl group there is coordinated directly to the metal ion, while the carbonyl group is H-bonded to a coordinated water molecule. In the trinuclear paac species the non-equivalence of both donor sites could be drowned by sterical factors since the close approach of the phosphonate sides of the terminal anions towards the central cation is prevented by the voluminous ethoxy groups.

The ligand geometry is analogous to that of the *O*-propyl ester of the 1-cyano-2-oxo-propylphosphonic acid determined in the neutral complex $Cu(CNpaac)_2$.[1] Table VII gives several examples of bond length variations in three types of phosphonate compounds: phosphonate esters as individual compounds, complexes in which the β-ketophosphonate ligands are neutral, and complexes in which the corresponding ligands are ionic.

As seen from the Table, the length of the P=O group is not significantly changed by coordination irrespective of the form of the ligand. By way of contrast, the length of the P–C bond seems to be dramatically influenced by coordination. The range of variation (1.812–1.832 Å) for non-coordinated phosphonates reduces to 1.784–1.792 Å for neutral β-ketophosphonate ligands and further to 1.695–1.734 Å for ionic ligands. The rearrangement of the acetyl bond lengths in the deprotonated ligands is consistent with elongation of the carbonyl C=O and shortening of the C–C bonds. Consequently, the π-electron distribution proposed by Brunette has to include the P atom as well, *i.e.*, the structure shown below should be anticipated.



The charge distribution in the $Zn(CNpaac)_3^-$ anion also influences the CN groups, judging from the shortening of the C(1)–C(4) bond length (Table VI). Comparison of the C(1)–C(4) bond lengths in $Cu(CNpaac)_2$ (1.40(1) Å) and $Zn(CNpaac)_3^-$ shows a lengthening of the latter. The fold angle along the O . . . O axis is 26.0(4)°. This is the greatest deviation from planarity known for chelate complexes of this type.

SUPPLEMENTARY MATERIAL

Tables of the observed and calculated structure factors, anisotropic thermal parameters for the nonhydrogen atoms for the structures (**1**) and (**2**), respectively, and hydrogen atom positional parameters for structure (**1**) are available from O.A.

REFERENCES

1. J. Macicek, O. Angelova, G. Petrov and M. Kirilov, *Acta Cryst.*, **C44**, 626 (1988).
2. O. Angelova, G. Petrov and J. Macicek, *Acta Cryst.*, **C45**, 710 (1989).
3. O. Angelova, J. Macicek and G. Petrov, *Inorg. Chem.*, in press (1991).
4. J.P. Fackler, *J. Chem. Soc.*, 1957 (1962).
5. Enraf-Nonius, *Structure Determination Package. SDP/PDP V3.0 Users Guide* (Enraf-Nonius, Delft, The Netherlands, 1985).
6. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, III Ed., (Wiley, New York. 1987), p. 249.
7. K. Nakamoto, P.J. McCarthy and A.E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).
8. K.E. Lawson, *Spectrochim Acta*, **17**, 248 (1961).
9. F.A. Cotton and R.A. Schunn, *J. Am. Chem. Soc.*, **85**, 2394 (1965).
10. J. Corset, *Pure Appl. Chem.*, **58**, 1133 (1986).
11. J.D. Baldeschweiler, F.A. Cotton, B.D.N. Rao and R.A. Schunn, *J. Am. Chem. Soc.*, **84**, 4454 (1962).
12. J.P. Brunette, L. Jurdy, M.J.F. Leroy and B. Allard, *Spectrochim. Acta*, **37A**, 991 (1981).
13. M. Burgard and J. Ceccaroli, *J. Chem. Phys.*, **86**, 4817 (1982).
14. T. Bottin-Strzalko, J. Corset, F. Fromet, M.J. Pouel, J. Seyden-Penne and M.P. Simmonin, *J. Org. Chem.*, **45**, 1270 (1980).
15. R.R. Shagidulin, A.V. Chernova, V.S. Vinogradova and F.S. Muhametōv, *Atlas of Infrared Spectra of Organophosphorus Compounds*, (Nauka, Moscow, 1984).
16. A. Yordanov and J. Macicek, *Coll. Abstr. 12th ECM, Moscow*, **3**, 196 (1989).
17. J. Macicek, Bulgarian Academy of Sciences, Sofia, Bulgaria, *JCPDS Grant-in-Aid Report* (1990).
18. E.L. Muetterties and L.J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).
19. T.M. Greaney, C.L. Raston, A.H. White and E.N. Maslen, *J. Chem. Soc., Dalton Trans.*, 876 (1975).
20. M.J. Bennett, F.A. Cotton and R. Eiss, *Acta Cryst.*, **B24**, 904 (1968).
21. F.A. Cotton, L. Hugel and R. Eiss, *Inorg. Chem.*, **7**, 18 (1968).
22. F.A. Cotton and B.H.C. Wuinquist, *Inorg. Chem.*, **9**, 688 (1970).
23. E. Weiss, J. Kopf, T. Cardein, S. Corbelin, U. Schumann, M. Kirilov and G. Petrov, *Chem. Ber.*, **118**, 3529 (1985).
24. S.M. Bowen, E.N. Duesler and R.T. Paine, *Inorg. Chim. Acta*, **61**, 155 (1982).
25. D.J. McCabe, E.N. Duesler and R.T. Paine, *Inorg. Chem.*, **24**, 4626 (1985).